Organic Leachates from Water Service Line Liners and Coatings and Their Fate in Drinking Water

By

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Submitted to the graduate degree program in Chemistry and the Graduate Faculty of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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Abstract

There is growing interest in using pipe lining and coating technologies to control corrosion and prevent release of metals (lead and copper) into drinking water from water service lines and from water pipes in homes, hospitals, hotels, and other buildings. Use of linings and coatings in small diameter pipes is expected to result in increased concentrations of any organic constituents able to leach into drinking water. Leaching of organic constituents from an epoxy coating and a polyethylene terephthalate (PET) liner, both potable water grade, was investigated using a fill-and-dump sampling technique employing long holding times to maximize the concentrations of leached constituents. Organic leachates of focus included bisphenols, bisphenol diglycidyl ethers (BDGEs), phthalic acids, and phthalate esters because these may pose endocrine disrupting risks when consumed. Analytical techniques included liquid chromatography/tandem mass spectrometry (MS), gas chromatography/MS, and time-of-flight MS. No phthalates were observed leaching from the PET liner; the epoxy coating leached low levels of bisphenol A (BPA), BPA-like compounds, and bisphenol A diglycidyl ether (BADGE).

Assessing drinking water safety requires not only identifying leachates but also understanding their reactions in drinking water that may lead to by-products formation. Hydrolysis and chlorination reactions (with free chlorine and monochloramine) were investigated under drinking water conditions. Hydrolysis of BDGEs and chlorination of bisphenols were found to proceed at rates that may significantly influence human exposure to these compounds and their by-products in tap water. To facilitate future health risk assessments (by others), key by-products were identified and kinetic models of these reactions were developed. The BADGE hydrolysis model estimates residual BADGE concentrations from

15 to 40 °C and pH 2 to 12; half-lives at pH 7 and 15, 25, and 40°C were estimated to be 11, 4.6, and 1.4 days respectively. The chlorination (free chlorine) model estimates residual BPA and bisphenol F (BPF) concentrations from 15 to 25 °C and pH 3 to 12, with estimated BPA and BPF half-lives (with 1 mg/L of free chlorine, pH 6 to 11, and 10 to 25 °C) estimated to be from 3 to 35 min.

This dissertation is dedicated to my brother:

SPC David Joseph Lane

1987-2007

And to all those who have given their lives for a greater good.

Acknowledgements

My journey through graduate school was only successful with the guidance and encouragement of so many people. The sacrifices and dedication of scientists before me created a strong scientific foundation that made my research possible. I am fortunate to live in a society where the pursuit of higher education is valued and encouraged.

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To my biggest fan, cheerleader, and best friend: my mom. For always providing a listening ear and believing in all I could become. Her observation of how passionate I was about

environmental topics was why she encouraged me to pursue a degree in environmental sciences. I would not be the person I am today without her!

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Chapter 1: An Introduction to Drinking Water Service Line Liners and Coatings

1.1 Drinking Water Service Lines

Drinking water service lines are the pipes that extend from the water main to the residential dwelling or commercial building. As illustrated in Figure 1.1, the portion of pipe from the water main to the property line is the responsibility of the city or municipality providing water, while the section of pipe from the property line to the building is generally the responsibility of the homeowner or business owner. A 1988 amendment to the Safe Drinking Water Act (SDWA), the Lead Contamination Control Act (LCCA), prohibited the use of lead service lines (LSLs) and limited the use of lead-containing products in drinking water distribution systems.[1,2] The SDWA and LCCA did not mandate removal of LSLs, except as noted below, and in regions of the U.S. with older cities (e.g., New England) some utilities still have many LSLs in place. An estimated 3.3 million LSLs were still in use in the U.S. during 1990.[3] Copper service lines (CSLs) have been used for the past few decades in water distribution systems due to the ease of installation, low cost, and corrosion resistance.[2] In 1994 approximately 80% of residential water pipes were CSLs.[4]

Water service lines are prone to metal leaching[5] (i.e., corrosion), which can cause detectable levels of lead and copper in drinking water. Due to concerns about public health and safety[6,7], the United States Environmental Protection Agency (EPA) instituted the Lead and Copper Rule (LCR), which establish drinking water action limits in tap water of 15 ppb (parts-per-billon or μg/L) for lead and 1,300 ppb for copper[8]. Drinking water providers are required to monitor lead and copper levels at the tap, and if the action level is exceeded in 10% of water samples, steps must be taken to lower the levels.[8]

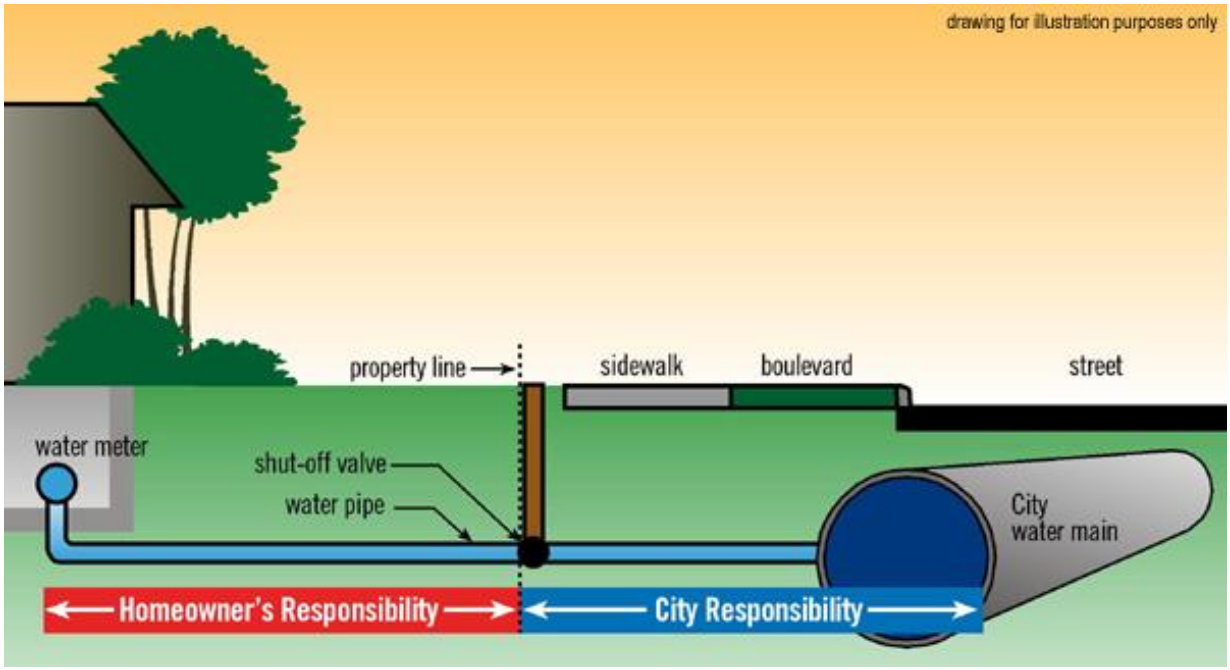


Figure 1.1 Cost responsibility of a water service line extending from the city water main to the building. Figure is the property of City of Winnipeg Water and Waste Department and used with permission.[12]

Lowering lead and copper levels in drinking water normally begins with a system assessment followed by optimized corrosion control and with pipe replacement as a final option. The water service line may be replaced from the water main to the building (full service line replacement) or only from the water main to the property line or to a utility-owned water meter or shut-off valve (partial service line replacement) (Figure 1.1).[9,10] If replacement becomes necessary, the water utility must replace their section or water service line but it is not mandatory for the homeowner to do so. A LSL replacement campaign by the EPA and DC Water (District of Columbia Water and Sewer Authority) found that disturbing pipes during replacement caused higher lead levels for months after replacement.[11,12]

Drinking water providers and homeowners are seeking rehabilitation technologies to prevent the high costs associated with full or partial pipe replacement, and internal pipe linings and coatings are being considered. Currently, the EPA does not view lining or coating technologies as an acceptable form of replacement once the action limit has been exceeded. However, utilities can voluntarily use these technologies before reaching the action limit, thus lowering lead and copper before mandatory replacement is required. The LCR is currently under review and could be revised to include rehabilitation technologies as an alternative to full or partial service line replacement.

1.1.1 Pipe Replacement and Rehabilitation Technologies

Traditional pipe replacement is termed Open Trench Replacement in which case a pipe is excavated and replaced at significant cost to the drinking water provider or homeowner.[3,13] DC Water estimates the minimum homeowner replacement cost is $2,500 for 20 feet of residential LSL.[14] Replacement on New Route and Replacement Using Existing Route are less

invasive pipe replacement techniques. Replacement on New Route leaves the old pipe in the ground and a trenchless technology is used to insert a new pipe. Replacement Using Existing Route uses pipe pulling to remove the old pipe and pull in a new pipe along the same route.[3] Although less invasive, these alternative still have moderate to high estimated costs ($320 to $2000 estimate), similar to those of open trench replacement.[13]

To reduce the costs of full or partial service line replacement, homeowners and utilities are seeking rehabilitation technologies that prevent heavy metal leaching, do not leach additional contaminants into the water, and withstand the test of time. Coatings are commonly applied to water mains and water storage tanks but their application to small diameter (0.5 to 1 inch) water service lines is a relatively recent development. Two major rehabilitation techniques, slip lining and pipe coating, are only applicable if the old pipe is structurally sound.[3] Slip lining is the placement of a close- or loose-fit liner into the aging pipe. Pipe coating involves application of a layer of material that, after curing, functions as a barrier between the old pipe and water. In terms of cost, slip lining has a low to moderate cost (e.g., $450 to $700 per installation) and pipe coating a moderate cost (e.g., $900 to $1100).[13] These cost estimates are only rough approximations and actual costs can vary depending on the specific replacement environment and what is included in the cost basis (e.g., the location and cost of digging access pits and whether traffic control and street repairs will be required). Table 1.1 lists materials used in commercially available pipe rehabilitation products.[3,16-21] Lining and coatings used in public water supply systems in the U.S. must normally be certified by the National Sanitation Foundation International (NSF) but the certification data are not readily available to consumers or water regulators. Polyethylene terephthalate (PET) liners and epoxy coatings are two

Table 1.1 Materials used for pipe rehabilitation techniques and some commercially available products.

Replacement Type	Material	Products and Suppliers*
Slip Lining, Close-Fit Liner	PE (polyethylene)	Wavin Compact Pipe
	PET (polyethylene terephthalate)	Wavin Neofit™
	HDPE (high density polyethylene)	Subline® and Polyline
Slip Lining, Loose-Fit Liner	HDPE: high density polyethylene	APTec HDPE Sliplining
	PEX: cross linked polyethylene	
Coating	epoxy	Nu Flow and Ace Duraflo®
	polyurethane and polyurea	3M™ Scotchkote™ Pipe Renewal Liner
	calcite coating	National Water Main Cleaning Company
	polyethylene/epoxy	PALTEM™

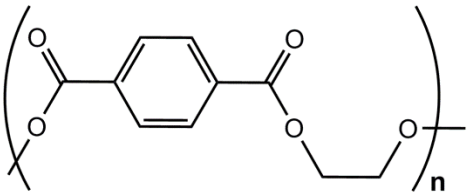
* This list is not intended to be exhaustive; other products and suppliers may be available for a given replacement type or material.

common pipe rehabilitation materials being considered for water service lines in the United States and are addressed in detail immediately below.

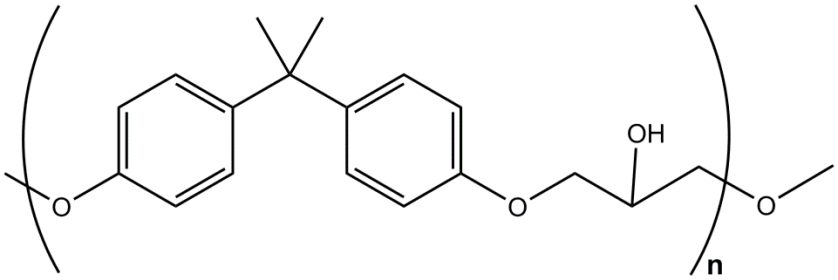
1.1.2 Polyethylene Terephthalate (PET) Pipe Liners

PET is a strong, lightweight, and relatively inexpensive plastic used in many consumer products and is identified by the resin code 1 ().[22] The formation of PET involves the reaction of terephthalic acid (TPA) or dimethyl phthalate (DMTP) with ethylene glycol to form the polymerized PET (Figure 1.2).[23] TPA is commonly used but phthalic acid (PA) and isophthalic acid (IPA) can also be polymerized and other diols (e.g., 1,4-butanediol and 1,4-dimethylolcyclohexane) can be used in place of ethylene glycol.[23]

PET's strong yet lightweight nature make it an attractive option for lining of drinking water service lines. Since it is a thermoplastic, PET can be softened under heat and pressure but become firm when cooled. This process can be repeated multiple times but continued remolding will cause degradation of PET.[24] For service line applications, a small diameter PET pipe is inserted into the old pipe and the PET is expanded to form a close-fit lining within the pipe (Figure 1.3). The installation process typically requires 13 minutes (excluding equipment setup and takedown time) and involves cleaning the internal surface of the pipe with foam swabs, inserting an unexpanded PET liner into the pipe, and running hot water (90 °C) through the liner while pressurizing (28 to 43 psi) it so that it expands.[3] Connection of the liner to end-fittings is important because improper seating of the liner could allow water to flow behind it, which could at least partially negate the benefit of the liner.[25]



PET



BADGE-Based Epoxy Resin

Figure 1.2 Chemical structure of PET prepared from terephthalic acid and ethylene glycol, where the n notates the degree of polymerization. Chemical structure of a BADGE-based epoxy resin prepared from bisphenol A and an epichlorohydrin.

Figure 1.3 PET liners: top two images show unexpanded PET liners, the bottom right image shows lined (right pipe) vs unlined (left) LSL pipe sections (with only the stainless steel end-fittings attached to them being visible), and the image on the bottom left shows PET-lined end-fittings attached to lead and copper service lines. (Images used by permission of Zachary Breault).

1.1.3 Epoxy Coatings

Epoxy coatings are formed through the polymerization of an epoxide containing resin.[26] Epoxies are made from a broad range of starting materials and have a range of physical properties (e.g., cure time, flexibility, and functionality). General epoxy characteristics desired for service lines include adherence to pipe surfaces, a short curing time, long-term durability, and low leaching. Historically, potable water grade epoxies have been used in the rehabilitation of water mains[27] but their use in drinking water service lines is a relatively new application.

Epoxy coatings for contact with potable water are formed from two main starting materials[25,28-30]: a resin prepolymer and a hardener. Epoxy formulations can also contain color pigments and fillers or extenders, with specific proprietary formulations varying by manufacturer. The resin prepolymer is designed to facilitate polymerization and is often a bisphenol with reactive epoxide side chains.[26] Common prepolymers are bisphenol A diglycidyl ether (BADGE) or bisphenol F diglycidyl ether (BFDGE). The diglycidyl ethers are formed through a reaction of bisphenol A (BPA) or bisphenol F (BPF) with an epichlorhydrin (Figure 1.2).[31] The epoxy mixture often contains novolac glycidyl ethers (NOGE) with approximately 30 to 40% 2-ring NOGE compounds (BADGE or BFDGE) and the remaining percentage is a mixture of 3 to 8-ring NOGE compounds.[32,33] Although BADGE is a common prepolymer ingredient, the epichlorohydrin can be reacted with other compound classes: phenols (BPF, tetrakis phenylolethane, resorcinol, methylolated phenol), alcohols (1,4-butanediol), phenolic resins (cresol, formaldehyde novolac), carboxylic and fatty acids, and nitrogen compounds (aniline).[26]

The hardener in epoxy coatings is often an ethyleneamine such as ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA),

or pentaethylenehexamine (PEHA). Ethyleneamines were the first hardeners used in epoxy chemistry due to their reactivity and short chain length between active sites (the unreacted epoxide groups) that enables a tightly cross-linked, three-dimensional polymerization structure.[31,34] In addition to the ethyleneamines, nitrogen, oxygen, and sulphur containing hardeners can also be used in epoxy chemistry.[35] Nitrogen curing agents include aliphatic amines, aromatic polyamines, cycloaliphatic polyamines, hydrazine, hydrazides, imidazols, tertiary amines (dimethylaminomethyl phenol or tris(dimethylaminomethyl) phenol), and ureas.[35] Oxygen curing agents include amino formaldehyde resins (urea-formaldehyde and melamine-formaldehyde resins), anhydrides, carboxylic acids, and phenol formaldehyde resins (phenol novolac resin or resole resins).[35] Sulphur curing agents include polysulphides and polymercaptans.[35] Additionally, compounds such as amine-boron trihalide complexes, quaternary phosphonium salts, and cationic salts (such as tri-arylsulphonium) have been used as curing agents.[35]

Application of epoxy coatings to service lines takes longer than installing PET liners since pipes must be sandblasted to create a rough surface[25] and epoxy curing times alone are significantly longer than the time required to install a PET liner. Specifically, a cure time is often estimated to be 5 to 16 hours and the entire coating process can take days[36]; even the two-hour curing time claimed by one manufacturer[37] is longer than the time required to install a PET liner. Epoxy application to service lines involves cleaning, coating, and curing steps. During the cleaning step the pipe is sandblasted (to remove any residues and roughen the surface to improve adherence of the epoxy), rinsed, and dried.[38] To coat the interior of the pipe an air pressure system spins the epoxy onto the walls of the pipe (Figure 1.4).[25] The final step is

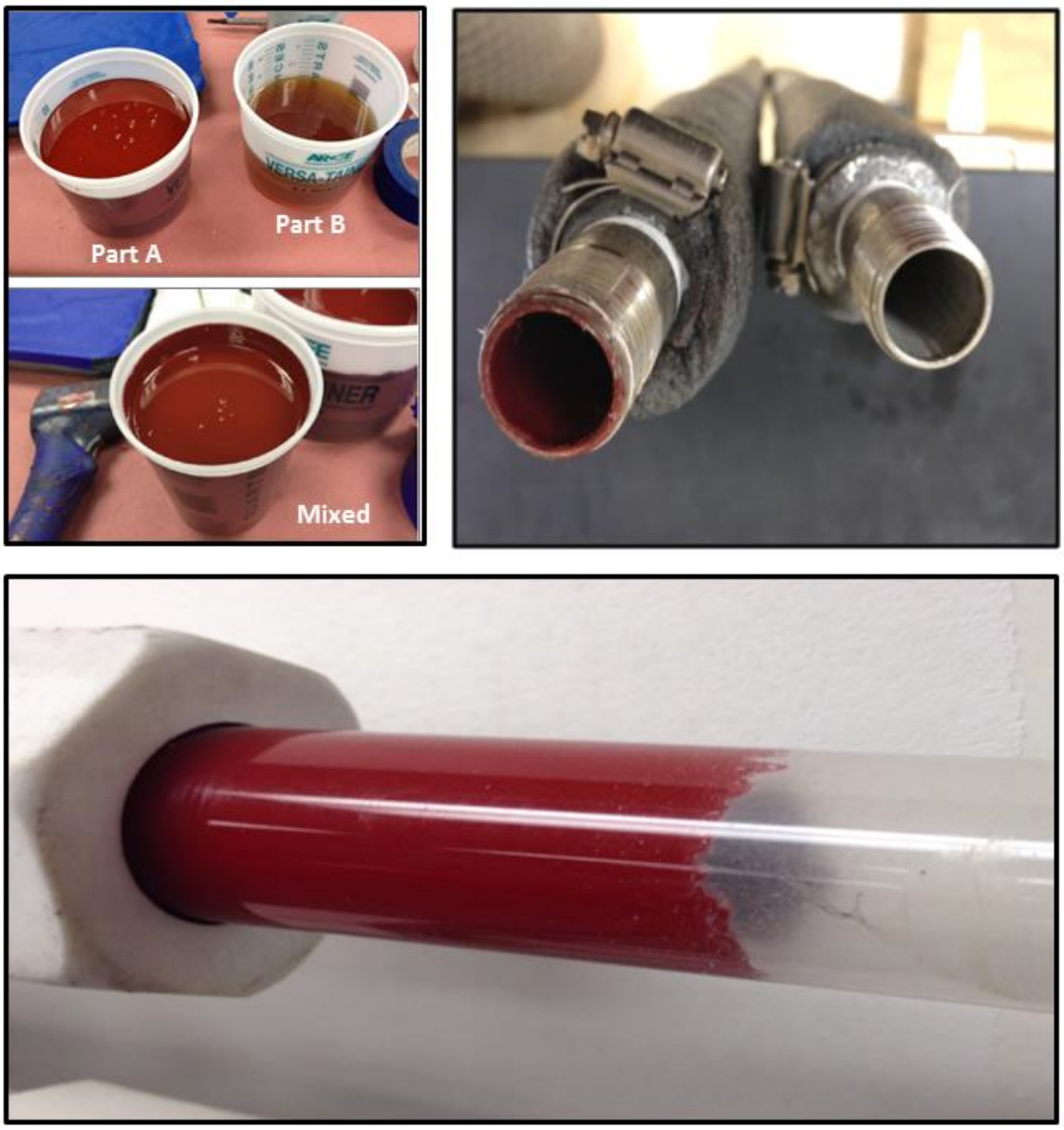


Figure 1.4 Potable water grade epoxy coating: top left are the part A and part B starting materials; top right are end-fittings attached to coated (left) and uncoated (right) pipe sections; and at the bottom is the epoxy being applied to a clear acrylic pipe. (Images used by permission of Zachary Breault).

allowing the epoxy to cure for an appropriate period of time and then rinsing the pipe with water to remove any remaining epoxy materials.[38] Manufacturers have worked to optimize the process such that coating over debris, blistering or bubbling, uncured epoxy, incomplete or thin coverage, ringing or ridging of the coating, slumping (buildup of epoxy), water damage, and holidays (i.e., pinholes or discontinuity) are minimized.[36]

1.2 Phthalate Leachates from PET

PET plastics can leach starting materials and phthalate esters (PAEs) of the phthalic acids (Table 1.2 and Figure 1.5). The wide range of possible leachates is attributed to the use of recycled PET. During prior use and during the recycling process, PET can adsorb many phthalates which can later leach into anything made from the recycled PET.[39,40] Washing steps can significantly reduce contaminants but are not mandatory in the recycling process.[41] While virgin PET minimally leaches PAEs, recycled PET is still widely used due to concerns about environmental waste.[40-42] Of the possible leachates, three phthalic acids and ten phthalate esters (checked in Table 1.2) are of specific interest for PET liners due to their prevalence of detection, regulatory concerns, and inclusion in EPA method 625[43].

1.2.1 Phthalate Stability in the Aqueous Environment

Phthalates are used in a wide variety of applications, thereby contributing a steady influx of phthalates into the aquatic environment. Phthalates are susceptible to hydrolysis but not under conditions found in aquatic environments. While phthalate hydrolysis is rapid at acidic and basic pH values, under drinking water conditions hydrolysis is slow with half-lives ranging from 3.2 to 2000 years (Table 1.2).[44] Photodegradation from the sun also provides a very slow mechanism of decay, with estimated of half-lives from 0.12 to 12 years.[44]

Table 1.2 Leachates from PET, regulated levels, and persistence in the environment.

PET Leachate	Abbreviation	CAS #	Reference	Leachates of Interest	EPA TAC† (ppb)	Hydrolysis Half Life (years)§
phthalic acid	PA	88-99-3	45, 46	✓		
dimethyl phthalate	DMP	131-11-3	43, 46-52	✓		3.2
diethyl phthalate	DEP	84-66-2	43, 46-51	✓	6000	8.8
dipropyl phthalate	DPP	131-16-8	51			
diallyl phthalate	DAP	131-17-9	51			
di-n-butyl phthalate	DNBP	84-74-2	43, 46-52	✓	700	22
diisobutyl phthalate	DIBP	84-69-5	51			
benzylbutyl phthalate	BBP	85-68-7	43, 47-50, 52	✓	1000	> 0.3
bis(2-ethylhexyl) phthalate	DEHP	117-81-7	43, 46, 48-54	✓	6*	2000
di-n-pentyl phthalate	DNPnP	131-18-0	51			
di-n-hexyl phthalate	DNHxP	84-75-3	51			
diphenyl phthalate	DPhP	84-62-8	51			
di-n-heptyl phthalate	DNHP	3648-21-3	51			
di-n-octyl phthalate	DNOP	117-84-0	48-50	✓		107
dinonyl phthalate	DNP	84-76-4	51			
diisononyl phthalate	DINP	28553-12-0	49		50	
di-n-dodecyl phthalate	DDP	2432-90-8	51			
diisodecyl phthalate	DIDP	26761-40-0	49			
isophthalic acid	IPA	121-91-5	45	✓		
dimethyl isophthalic acid	DMIP	1459-93-4	45	✓		
terephthalic acid	TPA	100-21-0	45	✓		
dimethyl terephthalate	DMTP	120-61-6	45	✓	700	
diethyl terephthalate	DETP	636-09-9	45	✓		
di(2-ethylhexyl)adipate	DEHA	103-23-1	43, 50-52	✓	400*	
4-nonylphenol	4-NP	104-40-5	47, 52			
4-tert-octylphenol	4-TOP	140-66-9	52			
ethylene glycol	EG	107-21-1	45			
formaldehyde	FA	50-00-0	55			
acetaldehyde	AA	75-07-0	55			

†EPA TAC = Total Allowable Concentration, as reported in reference 56
*EPA Maximum Allowable Concentration (MAC) values
§Half-life, as reported in reference 44

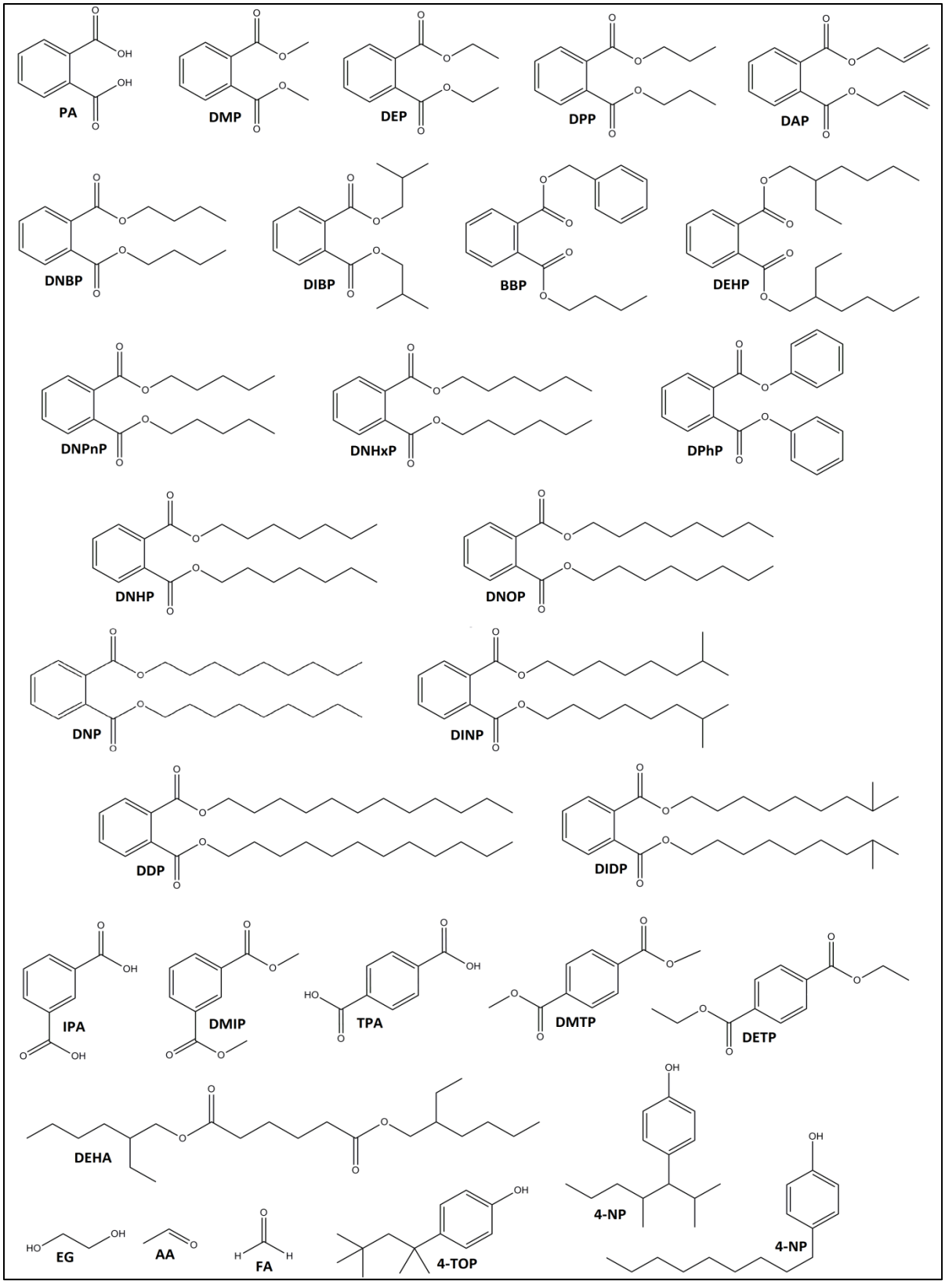


Figure 1.5 Structures of potential leachates from PET plastics.

Phthalates are degraded by aerobic and anaerobic bacteria with half-lives of less than a day to two weeks.[44] Biodegradation can remove long and short chain phthalates.[44]

1.2.1.1 Phthalate Reactivity in Drinking Water

While drinking water treatment can expose the phthalates to a variety of oxidants, there has not been reported decay of phthalates with oxidants typically used as disinfectants. Chlorine is a very common drinking water treatment chemical while other oxidants used include, monochloramine (MCA), ozone (O_3), chlorine dioxide, and hydroxyl radicals produced by advanced oxidation processes (AOPs).[57] Chlorinated by-products of phthalates have not been reported because the phthalates chemical structures are not conducive to chlorination reactions. AOPs that have been found to degrade phthalates are UV/H_2O_2, UV/H_2O_2/Fe, UV/TiO_2/O_3, UV/TiO_2, O_3, O_3/H_2O_2, O_3/UV, O_3/UV/TiO_2 (supported by γ-Al_2O_3), O_3/TiO_2, O_3/Ru-Al_2O_3, O_3/activated carbon, O_3/Fe, O_3/Fe-Silica (SBA-15), and O_3/zeolite.[58,59]

1.2.2 Regulation of Phthalates and Health Implications

In animal models, phthalates are carcinogenic and act as endocrine disrupters (but these effects are debated in humans).[60,61] Since phthalates leach from common everyday items, humans are chronically exposed to phthalates through ingestion, inhalation, and dermal routes.[60] Phthalates are metabolized to monoesters and oxidative products, eventually being excreted, and frequently detected, in urine.[60] Animal studies suggest that how phthalates affect the body depends on the specific phthalate, level of exposure, age, and gender.[60] Human studies have noted a correlation with higher levels of phthalates and asthma[62], pulmonary function[63], reproductive problems[60,64], embryonic development[60], and breast cancer[65]. None of

these studies have proved causation and some studies are controversial since chronic phthalate exposure makes it difficult to establish a control group with no phthalate exposure.

The EPA has a phthalate action plan in place for phthalates to address their manufacturing, processing, and distribution.[66] Further, the EPA has established total allowable concentrations (TAC) for DEP, DNBP, BBP, DINP, DMTP and maximum allowable concentrations (MAC) for DEHP and DEHA (Table 1.2). The European Commission's REACH regulation (Registration, Evaluation, Authorization and Restriction of Chemical substances) lists high molecular weight phthalates (e.g., DINP, DIDP) as not toxic to humans but still does not permit their use in toys or childcare articles; low molecular weight phthalates (e.g., DBP, BBP, DEHP, DIBP) are listed as toxic substances and not to be used in toys, childcare articles, or cosmetics.[67] The European Union has set specific migration limits for phthalates that range from 0.3 to 30 mg/kg of food simulant.[68]

1.2.3 Phthalate Detection Methods

Phthalates in biological, environmental, and food samples are analyzed using a wide range of analytical methods and techniques. Sample matrices influence the level of sample preparation, with food, biological, and wastewater samples requiring more preparation than drinking water samples. Techniques of focus for this method review will be phthalates in water and other aqueous samples. However, many of the techniques described herein can also be applied to food, biological, and other environmental samples.

Analytically, the challenge in measuring phthalates is preventing laboratory background levels and sample contamination. Phthalates are ubiquitous in the laboratory environment with contamination sources including air, water, solvents, reagents, glassware, syringes, syringe

filters, pipette tips, and equipment.[69-71] Measures can be taken to significantly reduce phthalate contamination and include avoiding contaminated lab tools, solvents, or reagents with phthalates, copious rinsing and solvent washing, and baking glassware at high temperatures (e.g., >400°C).[50,69,72-74] Frequent preparative and instrumentation blanks can help to monitor for sample contamination.[69]

Sample preparation techniques for phthalates include liquid-liquid extraction (LLE), solid phase extraction (SPE), solid phase microextraction (SPME), and stir bar sorptive extraction (SBSE). Historically, LLE was the most common sample preparation and preconcentration technique and is still seen in EPA Methods 506.1, 625, 606, and 8061A.[50,72-74] The solvent used in the extraction depends on the phthalates of interest and the detection method desired. Lower molecular weight phthalates are polar, while higher molecular weight (longer chain) phthalates tend to be non-polar. To aid in partitioning of polar phthalates into the organic phase, salt can be added to the sample.[50,75-77] The salting-out phenomenon effectively changes the solubility of the analytes, encouraging them to transition into the organic phase.[78]

Solvents that can be used for LLE phthalate extraction include acetonitrile[79], cyclohexane[69,76,80], dichloromethane[48,55,76,80-82], dichloromethane/cyclohexane[76], diethyl ether[81,80], ethyl acetate[81], hexane[76,80,81,83] , hexane/dichloromethane[75], methylene chloride[50,72-74], propanol[79], and toluene[76,81]. To overcome the LLE disadvantage of large solvent volumes, techniques have been developed for phthalates that reduce both the sample and solvent volumes. These techniques include homogeneous liquid-liquid extraction (HLLE)[84], liquid phase microextraction (LPME)[85], dispersive liquid-liquid microextraction (DLLME)[86], along with the associated techniques of: temperature-controlled ionic liquid DLLME[87], low-density solvent

(LDS)-DLLME[88], magnetic stirring assisted (MSA)-DLLME[89], vortex-assisted surfactant-enhanced-emulsification (LDS-VS)-LLME[90], and air-assisted (AA)-DLLME[91].

SPE is a preparation technique with small solvent volumes and the ability to extract a wide range of analytes. Common sorbent materials for phthalates are listed in Table 1.3 and elution from the sorbents can be performed with acetone[83], acetone/ethyl acetate[92], acetonitrile[76,83,93-95], acetonitrile/methanol[76], dichloromethane[96], dichloromethane/hexane[47,97], diethyl ether[83], diethyl ether/methanol[98,99], methanol[76,100], ethyl acetate[76,83,82,101], ethylacetate/methanol[76], hexane[83], hexane/diethyl ether[83], methanol[102-104], and methanol/dichloromethane[47,105]. Selection of the elution solvent depends on the sorbent material and specific phthalates of interest. Although commonly used singly and offline, cartridges can be used in series[92,103] and automated online[93] with the detection method. Less common SPE applications have been explored including: miniaturized fiber-in-tube SPE[106] (similar to SPME); preconcentration of phthalates on *Saccharomyces cerevisiae* immobilized silica gel[107]; and cartridges packed with multi-walled carbon nanotubes[108], ionic liquid mixed hemimicelle[110,109], or aerosol-OT–γ-alumina admicelles[111].

SPME has been explored for phthalates because it eliminates both organic solvents and the long analysis times of LLE and SPE. During SPME, a polymer-coated fiber is inserted into the liquid sample or headspace, where the analytes are adsorbed during sample extraction. The fiber is then withdrawn from the sample, inserted into a suitable injection port, and heated to desorb the analytes from the fiber for GC or LC analysis. A wide range of SPME fibers have been

Table 1.3 Solid phase extraction (SPE) cartridge sorbent materials for phthalate sample preparation.

Sorbent	Phase	Cartridge	Reference
C8 chains (silica-based)	reverse phase	Bakerbond™ SPE Octyl Biotage Isolute® C8	83, 92
C18 chains (silica-based)	reverse phase	Bakerbond™ SPE Octadecyl Biotage Isolute® C18 Merck Millipore LiChrolut® RP-18 Supelco LC-18 SPE	76, 83, 98, 99, 103
hydroxylated PS-DVB	reverse phase	Biotage Isolute® ENV+	81, 95, 99, 105
PS-DVB	reverse phase	Biotage Isolute® 101 Merck Millipore LiChrolut® EN Waters Sep-Pak LS-2 Supelclean™ EnviChrom P	81, 93, 94, 96, 97, 103
poly(divinylbenzene-*co*-*N*-vinylpyrrolidone	reverse phase	Phenomenex Strata™-X Water's Oasis® HLB	47, 97, 99, 100-102, 104
Florisil	reverse phase	Bakerbond™ SPE Florisil Supelco Florisil®	76, 83

PS-DVB = polystyrene-divinylbenzene
Florisil = blend of magnesium oxide and silica gel

investigated for pthalates and the materials that provide the best results are CW/DVB(carbowax/divinylbenzene)[112-114], DVB/CAR(carboxen)/PDMS(polydimethylsiloxane)[115], PA (polyacrylate)[115-118], PDMS[115,117-120], and PDMS/DVB[46,112-114,121,122]. The range of fiber materials used stems from the polarity differences among the phthalates. PDMS is non-polar and generally better for the higher molecular weight phthalates (e.g., DNOP, DNP, DEHP), while PA and CW/DVB are polar and better for low molecular weight phthalates (e.g., DMP and DEP), and PDMS/DVB and DVB/CAR/PDMS are bipolar and best for mid-molecular weight phthalates (e.g., DBP and BBP).[119,123]

SBSE (stir bar sorptive extraction) is similar to SPME in that a polymer coating provides capture of the analytes. During SBSE, a stir bar coated with a PDMS polymer[124-126] is stirred in the sample where it adsorbs phthalates, then removed from solution and heated or extracted to desorb the phthalates for analysis. The advantage of SBSE is that the stir bar has a larger polymer surface area (in comparison to SPME) and stirring increases the sample/polymer contact area and accelerates adsorption, resulting in better recovery and sensitivities.

The two common separation and detection methods for phthalates are gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS). Historically, GC/MS was frequently used in environmental analysis because it could analyze complex samples, quantitate known compounds, and identify unknowns. GC columns used for the separation of phthalates include non-polar columns composed of (5%-phenyl)-methylpolysiloxane[47,69,81-83,85,88,90,92,93,96,97,99-101,113,116,118,119,123,125-130] and mid-polarity columns composed of (20% phenyl)-methylpolysiloxane[46], (50%-phenyl)-methylpolysiloxane[103], or (35% phenyl)-methylpolysiloxane[117]. The MS ionization technique frequently used for phthalates is

electron ionization (EI)[46,47,69,81,,82,85,88,90-93,96,97,99-101,103,113,116,118,119,123,125-130] but electron capture (EC)[83,117] has also been used. MS detection can monitor specific phthalate ions through single ion monitoring (SIM)[46,47,69,81,85,88,90,96,97,99,100,119,123,126,127,129] or scan for a wide range of phthalates[47,82,91-93,96,100,103,113,116,118,125,128,130]. Quadrupole ion trap[82,113] and triple quadrupole[101] mass analyzers, along with thermal desorption (TD)-GC[124] and large volume injection-programmed temperature vaporization (LVI-PTV)-GC[124] have also been used in the analysis of phthalates.

LC/MS is widely used in environmental analysis since it reduces sample preparation time and provides low-level quantitation. With GC, analytes must be converted from the aqueous sample into an organic phase for injection, whereas relatively clean aqueous samples can be directly injected into an LC. Reverse phase columns that have been used for phthalates are C8[86,98,108,131] and C18[55,75,79,87,93,95,98,102,104,106,107,109-111,114,121,132-136]. Elution from the column has been done isocratically with mobile phases including acetonitrile (ACN)[104,114], ACN/water[55,108,109,111,121], ethanol/water[107], or methanol(MeOH)/water[86,87,107,106,132] and using gradient elution with 0.1 to 0.5% acetic acid/ACN[93,94,98,131], water/ACN[75,79,95,102,133,134], or water/MeOH[110,135]. MS ionization techniques include atmospheric pressure chemical ionization (APCI)[94,95,98,110] and electrospray (ESI)[93,98,131]. Quadrupole mass spectrometers allow scans[94,95,98,110], SIM[93,95,98,131], or multiple reaction monitoring (MRM)[93,95,98,131] analysis of phthalates; time-of-flight (TOF) MS[102] analysis has provided phthalate data with high mass resolution.

Other detection methods for phthalates include GC/flame ionization detector (FID)[76,77,84,91,118,137] and LC/UV[55,75,79,87,89,94,106-109,111,114,121,133-136]. Both of these methods tend to

have higher detection limits when compared to MS and are impractical for low-level phthalate analysis. GC columns used with FID are non-polar 100% dimethyl siloxane[91] or (5%-phenyl)-methylpolysiloxane[76,77,84,137,138] and polar ionic liquid columns[118]. Columns described for LC/MS are also used in UV applications. Diode array detectors (DAD)[108,109,133,134] and variable wavelength detectors (VWD)[86,132] have been used with detection wavelengths ranging from 203 to 360 nm[55,75,79,87,89,94,106,107,111,114,121,135,136].

1.3 Bisphenol Leachates from Epoxy Coatings

Bisphenol A (BPA) has been reported leaching from epoxy coatings into a wide variety of foods and beverages (e.g., milk[139-141], soft drinks[142,143], mineral water[143,144], drinking water[143,145], and wine[146,147]). Although canned food products are a common source of BPA[148-156], it has also been found in non-canned food items (e.g., cereals[157], honey[158], meats[159], eggs[139], and powdered and liquid infant formulas[154,160,161]). Leached concentrations in canned products depend on storage temperatures[148], type of material in contact with the epoxy[150], product expiration date[150], specific product lots and manufacturer[149], and contact with equipment that processes food prior to canning[162].

Compounds other than BPA can leach from epoxy, including those listed in Table 1.4. BADGE is the reactive form of BPA in many epoxy starting materials and also leaches into canned foods products[163-173]. Due to public concern over BPA leaching, epoxy manufacturers are seeking structurally similar bisphenol alternatives (Figure 1.6 and 1.7), such as bisphenol B, D, E, F, and S (BPB, BPD, BPE, BPF, BPS).[142,174,175] BPF[130,175,176] and BFDGE[166,168-170,173] (the reactive prepolymer, bisphenol F diglycidyl ether), have been observed in foods and the environment, indicating that some manufactures are starting to use BPF as an alternative

Table 1.4 Bisphenol and bisphenol diglycidyl ether epoxy leachates and by-products.

Leachate	Abbreviation	CAS #	Primary Source*
bisphenol A	BPA	80-05-7	resins
monochlorobisphenol A	BPA-Cl	74192-35-1	resin by-product
dichlorobisphenol A	BPA-2Cl	79-98-1	resin by-product
trichlorobisphenol A	BPA-3Cl	40346-55-2	resin by-product
tetrachlorobisphenol A	BPA-4Cl	79-95-8	resin by-product
bisphenol B	BPB	77-40-7	resins
bisphenol D	BPD	6807-17-6	paper
bisphenol E	BPE	2081-08-05	resins
bisphenol F	BPF	620-92-8	resins
bisphenol S	BPS	80-09-1	paper
bisphenol A diglycidyl ether	BADGE	1675-54-3	resins
bisphenol A (2,3-dihydroxypropyl) glycidyl ether	BADGE-H2O	76002-91-0	resin by-product
bisphenol A bis(2,3-dihydroxypropyl) ether	BADGE-2H2O	5581-32-8	resin by-product
bisphenol A (3-chloro-2-hydroxypropyl) (2,3-dihydroxypropyl) ether	BADGE-H2O-HCl	227947-06-0	resin by-product
bisphenol A (3-chloro-2-hydroxypropyl) glycidyl ether	BADGE-HCl	13836-48-1	resin by-product
bisphenol A bis(3-chloro-2-hydroxypropyl) ether	BADGE-2HCl	4809-35-2	resin by-product
bisphenol F diglycidyl ether	BFDGE	2095-03-6	resins
bisphenol F (2,3-dihydroxypropyl) glycidyl ether	BFDGE-H2O	303733-72-4	resin by-product
bisphenol F bis(2,3-dihydroxypropyl) ether	BFDGE-2H2O	72406-26-9	resin by-product
bisphenol F (3-chloro-2-hydroxypropyl) (2,3-dihydroxypropyl) ether	BFDGE-H2O-HCl	638193-72-9	resin by-product
bisphenol F (3-chloro-2-hydroxypropyl) glycidyl ether	BFDGE-HCl	374772-79-9	resin by-product
bisphenol F bis(3-chloro-2-hydroxypropyl) ether	BFDGE-2HCl	194672-61-2	resin by-product

*resin by-product = leached BPA, BADGE, BPF, or BFDGE that has formed a by-product in solution

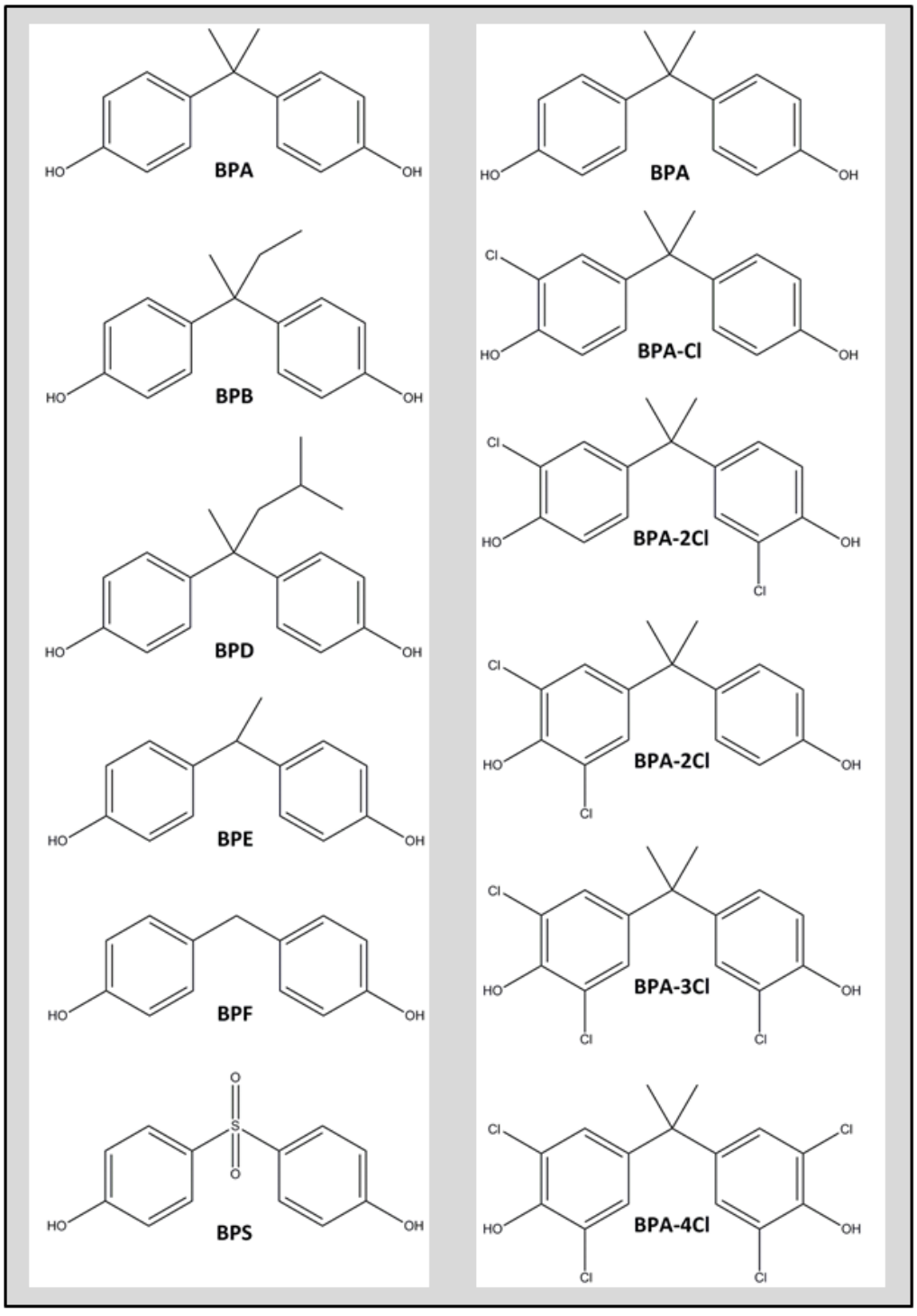


Figure 1.6 Structures of selected bisphenol epoxy leachates and chlorinated BPA by-products.

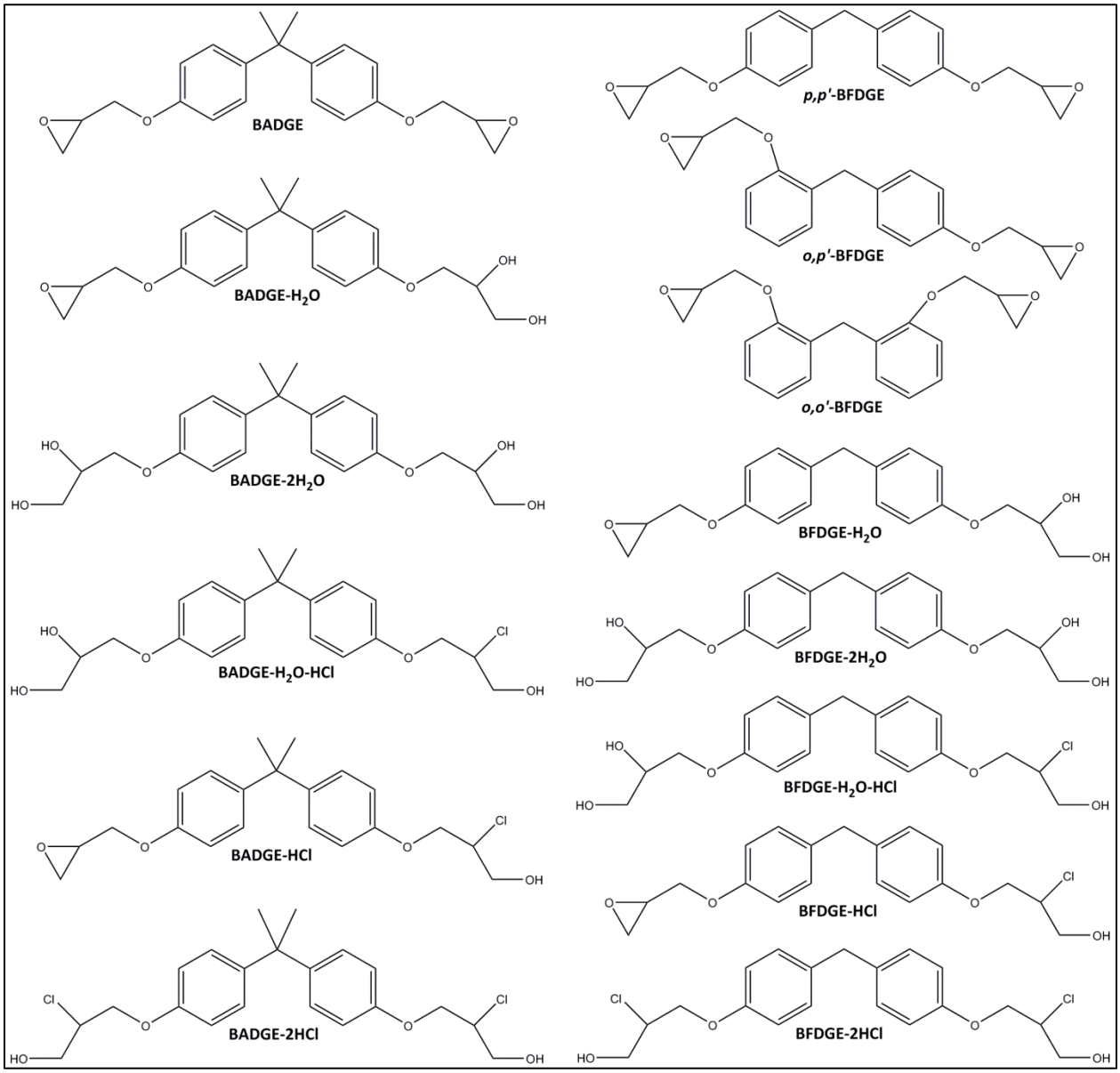


Figure 1.7 Structures of selected bisphenol diglycidyl ether epoxy leachates and related by-products.

starting material. BPS and BPE have also been detected in the environment but with less frequency than BPF.[176,177]

The coatings being applied to water service lines are structurally similar to food can epoxy coatings. All the leachates of interest for epoxy can coatings (Table 1.4, Figures 1.6 and 1.7), are also of interest as potential leachates from potable water grade epoxy. Due to in-pipe curing, the epoxy coating has a greater potential for leachates when compared with pipe liners not cured in place (e.g., PET liners). There is preliminary data demonstrating that BPA and BPF can leach from potable water grade epoxy.[178,179] By-products and reactions that can occur after leaching will be discussed in Section 1.3.1.1.

1.3.1 Bisphenol Stability in the Aqueous Environment

Due to the use of BPA in many applications, it is considered a pseudo-constant contaminant in the environment.[180,181] This means that, in aqueous environments, BPA undergoes biodegradation and photodegradation but with influxes from so many sources, detectable levels of BPA are often present in the environment (when using instruments of sufficient sensitivity). Reported aqueous levels of BPA are listed in Table 1.5 along with the levels reported in sediments (as BPA can partition into sediment layers[182]). Levels in surface waters vary and are influenced by physical locations such that in close proximity to a landfill or a specific manufacturing facility higher levels of BPA have been reported.[180] Biodegradation is the major decay mechanism for BPA in aquatic systems.[183] Microbial degradation can occur with specific strains of bacteria or fungi and with certain plankton species.[184] Bacterial decay of BPA occurs under abiotic or biotic conditions and is affected by bacterial counts and water temperature.[184,185] The average BPA bacterial degradation half-life is 5 days[184] but can range

Table 1.5 Reported levels of BPA and BPF in environmental waters and sediments

Water Type	[BPA], ppb	[BPF], ppb	Reference
rivers/surface Water	ND to 21	0.0001 to 0.18	130, 180, 186-190
US rivers/surface water	ND to 12		186, 191-194
U.S. stormwater canals	ND to 1.6		191
tap water	0.015 to 0.063		186
U.S. drinking water	ND to 0.044		192, 194
seawaters	ND to 2.5		186, 187, 195-197
wastewaters	0.018 to 5.0	0.022 to 0.123	130, 186
U.S. wastewaters	0.006 to 3.8		186
river sediments	ND to 10500	1.2 to 7.3	130, 186, 188-190
U.S. river sediments	1.5 to 800		186

ND = non-detectable ppb = μg/L for water and μg/kg (or ng/g) for sediments

from 2 to 20 days[185]. This also has implications for laboratory analysis since any bacterial growth in samples causes BPA decay. Therefore, sample storage at cold temperatures or the addition of suitable growth inhibitor is recommended to reduce BPA degradation.[198]

Photodegradation of BPA in aquatic systems also occurs and depends on water conditions and the amount of sunlight with estimated half-lives from 3 to 160 days.[182] Treatment methods for wastewater[183] and drinking water[199,200] have also been shown to degrade or reduce levels of BPA. Chlorination of BPA is the most relevant process and will be discussed in the following section. Aqueous stability of the other bisphenols (i.e., BPB, BPD, BPE, BPF, BPS) has not been explored but should be comparable to BPA due to their structural similarity.

The bisphenol diglycidyl ethers (BDGEs) have not been explored in terms of biodegradation, photodegradation, or water treatment processes. Due to the epoxide group of the BDGEs, they are susceptible to hydrolysis and have six known by-products: BADGE-H_2O, BADGE-$2H_2O$, BADGE-H_2O-HCl, BFDGE-H_2O, BFDGE-$2H_2O$, and BFDGE-H_2O-HCl (Figure 1.7). These by-products have been reported in many canned foods[164-167,173] and at temperatures above 40 °C reported BADGE half-lives range from 9 to 43 hours[201-203] and from 12 to 52 hours for BFDGE[204]. Hydrolysis of bisphenols is not expected because their functional groups do not facilitate hydrolysis reactions.[183]

1.3.1.1 Bisphenol Reactivity in Drinking Water

BPA has been detected in drinking water and in many surface waters that serve as sources of drinking water (Table 1.5). Drinking water treatment processes expose BPA to the chemicals used for disinfection. Chlorine, chlorine dioxide, and ozone are frequently used for

disinfection and oxidation of drinking water.[46] Potassium permanganate is often used to oxidize iron, manganese, and sulfides but has little disinfecting power and reacts to only a very limited extent, if at all, with organic contaminants. UV disinfection is becoming increasingly common, but the light intensities used for disinfection have little or no effect on most chemical contaminants. Since chlorine is by far and away the most commonly used chemical disinfectant/oxidant, chlorination will be the focus of the remainder of this discussion.

Chlorine can be applied as a primary (in-plant) or secondary (distribution system) disinfectant. Drinking water treatment facilities use primary disinfectants to provide strong initial disinfection.[205] Secondary disinfectants are typically weaker disinfecting agents (and weaker oxidants) stable enough to remain in the drinking water during its journey to faucet taps.[205]

Chlorination is a complex process since it can involve many different chlorine species. Hypochlorous acid (HOCl) is the chlorine species most heavily relied on for strong primary disinfection. The hypochlorite ion (OCl^-) is much less effective as a disinfectant, but is the dominant species at higher pH values. The sum of HOCl and OCl^- is referred to in practice as free chlorine[206], i.e., chlorine that is not combined with ammonia. It is important to note that this definition of free chlorine is based on the assumption that in dilute aqueous solution HOCl and OCl^- are the dominant chlorine species. A more rigorous definition of free chlorine might include other chlorine species, such as Cl_2, Cl_3^-, and H_2OCl^+ ; these other species are almost always ignored because their concentrations in dilute aqueous solution are negligible.[206] Relationships among chlorine species are shown in Figure 1.8.

Of the two chlorine species HOCl and OCl^-, HOCl has much greater disinfectant strength.[207] The acid dissociation constant (pK_a) for HOCl is 7.54 at 25°C.[208] Thus, disinfection is strongly pH dependent over the pH range of interest in drinking water treatment, and free chlorine is a stronger disinfectant at lower pH values. To compensate for this, longer contact times are used at higher pH values; and EPA has established minimum values of concentration times (CT values) that must be met to provide adequate disinfection under various sets of conditions (pH, temperature, the target organism, and the desired level of inactivation).[209] In the context of drinking water, chlorine concentrations are nearly always expressed in the equivalent units of mg/L as Cl_2. Since this research project was designed primarily to serve the drinking water community, chlorine concentrations will be reported in mg/L as Cl_2 (as opposed to molarity, mol/L, or equivalents per liter, preferred in other fields of chemistry).

A common secondary or residual disinfectant is monochloramine (MCA). MCA is a weaker disinfectant than HOCl and is formed by combining HOCl with ammonia (NH_3).[207] Di- and tri- chloramine also form when chlorine is combined with ammonia, but efforts are made to minimize these species because they impart a chlorinous taste to the water. To minimize their formation, MCA is typically generated with a Cl_2:N mass ratio of 3:1 to 5:1 and at a pH of 8 to 9. Chloramine formation is a complex system, with some species still not identified (Figure 1.8)[210]; and equilibrium may not be attained rapidly under some conditions, including some conditions relevant to drinking water treatment, so the concentrations of chloramine species present may change over time. When MCA is the dominant species, there are still trace levels of the other species in equilibrium (or proceeding toward equilibrium) with MCA. For simplicity, solutions prepared and used under conditions that maximize MCA formation will herein be

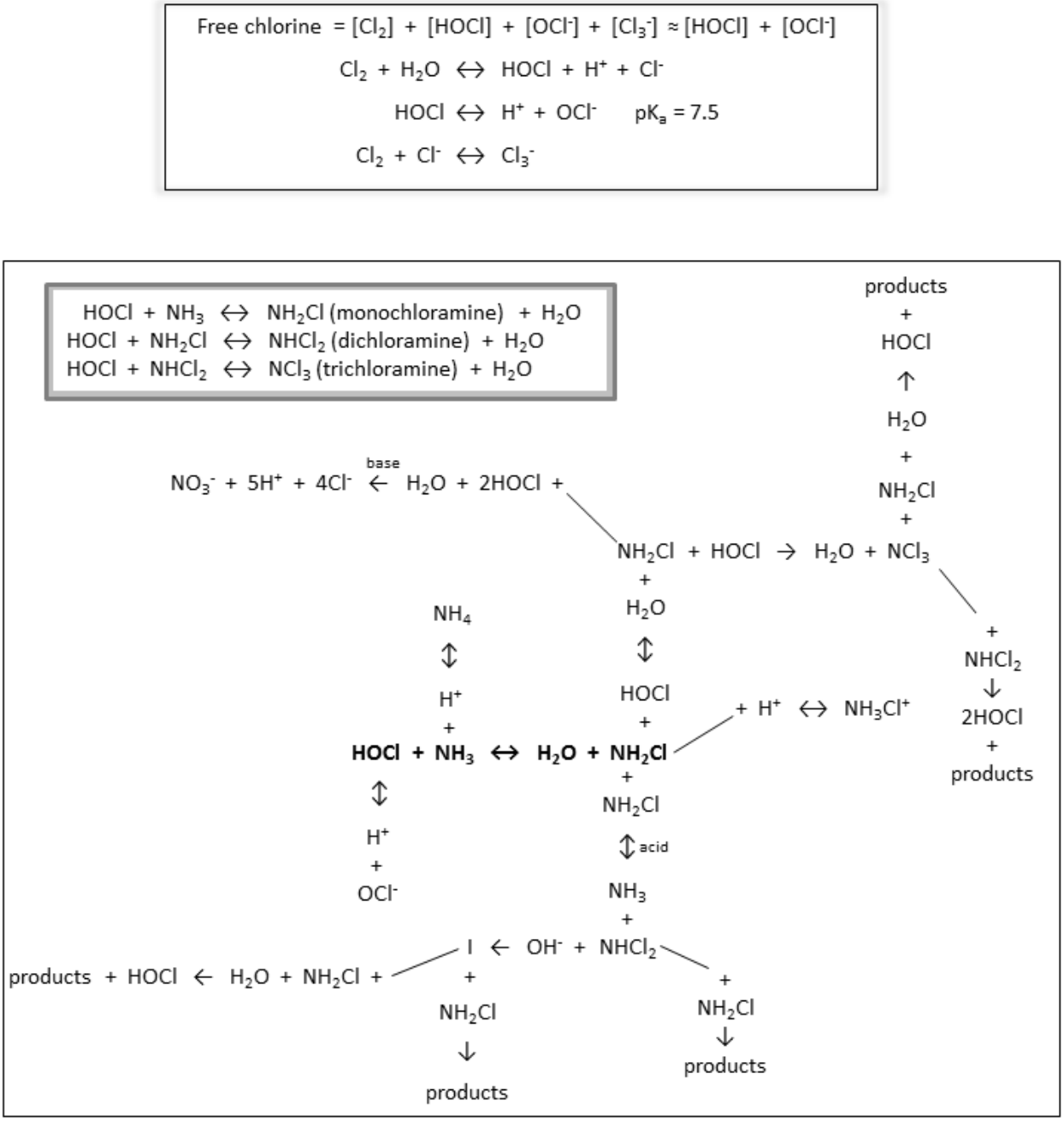


Figure 1.8 Reactions associated with free chlorine and combine chlorine. For reactions of chloramines, "I" represent unknown intermediates, "products" are unknown or unspecified products, and the inlayed box shows simplified key reactions. Adapted from the work by Jafvert and Valentine[210].

referred to as MCA solutions (and the other chloramine species will be ignored). Chloramines are referred to in practice as combined chlorine.

Bisphenol A is susceptible to halogenation reactions. Chlorinated by-products of BPA include mono-, di-, tri-, and tetra-chloro BPA (BPA-Cl, BPA-2Cl, BPA-3Cl, BPA-4Cl, Figure 1.6) as well as the degradation product trichlorophenol (TCP).[211-214] These chlorinated by-products have been detected in drinking water treatment facilities[213,214], drinking water[215], and water drawn from epoxy-coated drinking water pipes[179]. Chlorination of BPA with free chlorine has been modeled at various pH values (20°C) and the BPA half-life with a chlorine residual of 0.2 mg/L as Cl_2 was 1.5 hours.[216] Reactivity of BPA with MCA has not been previously reported and data was not found pertaining to chlorination of bisphenols similar to BPA (i.e., BPB, BPD, BPE, BPF, and BPS).

There are also chlorinated by-products of the BDGEs (i.e., BADGE-H_2O-HCl, BADGE-HCl, BADGE-2HCl, BFDGE-H_2O-HCl, BFDGE-HCl, BFDGE-2HCl, all depicted in Figure 1.7) that have been detected in canned foods.[164-167,170,173] The mechanism of BDGE chlorination with free chlorine or chloramines has not been reported. Similarly, neither the analysis of BDGEs in water or drinking water nor kinetic modeling of BDGE chlorination have been reported.

1.3.2 Regulation of Bisphenols and Health Implications

Public concern about BPA increased sharply in 2008 when Health Canada listed the endocrine disrupting chemical as a toxic substance.[217] This was especially concerning to the general public since BPA is used in many food packaging materials and containers (at the time including baby bottles). Leached BPA levels in food products and drinking water are typically below the EPA[218] and European Food Safety Authority[219] recommended BPA oral reference

dose or daily intake limit of 0.05 mg/kg bw/day (mg per kg of body weight per day). However, chronic low-level exposure to BPA has resulted in detection of BPA in human serum[220-228], plasma[226,229] (including fetal (cord) serum and plasma[222,227,230-232]), placental serum[230,233], amniotic fluid[222,234,235], breast milk[233,236-238], saliva[239], and urine[240,241]. These and other detections of BPA, including those in environmental samples discussed earlier, reinforced public concerns; this led to increased scrutiny of BPA by regulators and inspired scientific studies of BPA's potential human health effects.

BPA is xenoestrogen, i.e., a chemical foreign to the body that imitates estrogen upon entering the body. Specifically, BPA binds to and activates human estrogen receptors, as well as the thyroid hormone receptors and the peroxysome proliferator-activated receptor gamma.[148,242] Animal studies have shown a negative effect on the prostate, immune system, mammary glands, reproduction, brain development and behavior, and metabolism. Additionally, correlations have been made to cardiovascular disease, diabetes, obesity, and exacerbation of migraine symptoms[243-245]. Human studies with BPA have not determined causation but have examined correlations between elevated BPA levels and disease states. Correlations have been made with respect to negative impacts on reproduction, neurobehavioral development, and metabolic diseases (e.g., obesity, diabetes, heart disease, thyroid and liver function)[242,246,247], and, more specifically, to implantation failure during in-vitro fertilization[248], premature delivery[249], low birth weight[242], childhood asthma[250], insulin resistance[251], obesity[251], cardiovascular disease[246,252], high blood pressure (hypertension)[253,254], and thyroid function[242].

There is currently debate about the health risk related to chronic low-level BPA exposure. Some researchers, such as Frederick S. vom Saal, argue that this low-dose exposure is relevant and of concern.[243,255] However, neither the U.S. Environmental Protection Agency[218] (EPA) nor U.S. Food and Drug Administration[256] has chosen to regulate BPA. BPA did not meet EPA's screening criteria for inclusion on the third candidate contaminant list (CCL3)[218] for future drinking water regulations, nor is it included in the draft of the fourth list (CCL4)[257]. The National Sanitation Foundation (NSF) recommends a BPA drinking water criterion of 0.1 mg/L total allowable concentration and 0.01 mg/L single-product allowable concentration.[56]

The other bisphenols (i.e., BPB, BPD, BPE, BPF, BPS) have also demonstrated estrogenic activity. A key factor affecting estrogenic activity is length between the hydroxyl groups and the functional groups on the bridging carbon.[258,259] Using induced estrogenic activity as a measure, BPB appeared to exhibit the greatest activity, followed by BPA, BPE, BPF, with the lowest response produced by BPS. Knowing that manufacturers are considering using (or are already using) these other bisphenols, several studies have recently looked for (and found) BPS, BPF, and BPB in urine.[260-262] For example, in urine samples from 100 anonymous U.S. adults, BPA was detected in 95% of samples, BPS in 78%, and BPF in 55%.[261] The EPA is currently not considering any regulations for these bisphenols.

There is concern that the chlorination of bisphenols could cause a change in their toxicity. BPA-Cl and BPA-2Cl have greater estrogenic activity (higher human α-estrogen receptor affinity) than BPA.[190] Chlorinated BPAs have been detected in drinking water[179,215], which presents concerns about consumption. Consumption has resulted in detectable levels of chlorinated BPA by-products in human tissue, urine, and colostrum.[263] Currently, the U.S. does

not regulate the chlorinated bisphenols and further information (both occurrence and toxicity data) will be needed to support drinking water risk assessments.

While BDGEs do not follow the same biological pathways as BPA, there are concerns about their mutagenicity[163,264], genotoxicity[163,264], and anti-androgenicity[265]. Human exposure to BDGEs and BDGE by-products comes mainly from canned foods[164,165,266] and the environment[267]. A recent study found a correlation between the detection of BPA and BADGE in urine; every time BPA was detected in urine, BADGE was also present.[268] While there is some evidence of BADGE in human plasma[226,229], most human studies have focused on BPA, and the presence of BADGE in the body could be under-reported. Due to concerns with the consumption of canned food products, the European Union has established a 9 mg/kg food migration limit for BADGE and its hydrolysis products and a 1 mg/kg food migration limit for the chlorinated BADGE by-products.[269] BDGEs and BDGE by-products are not regulated in the U.S. but the NSF recommends a BADGE drinking water criterion of 1 mg/L total allowable concentration and 5 mg/L short term exposure level.[56]

1.3.3 Bisphenol Detection Methods

Bisphenol A has been detected in biological, environmental, and food samples. Due to interest in detecting BPA in diverse sample types, a broad array of sample preparation and quantitation techniques have been developed. This review will be limited to water, wastewater, and aqueous food matrices. Many of the techniques described can be used for biological, food, and other environmental (i.e., dust, air, etc.) samples but may require additional sample preparation.

Similar to phthalate detection, the challenge in BPA analysis is minimizing background BPA levels. The frequent use of BPA in plastic materials and laboratory equipment results in persistent background levels. BPA has been detected in water, solvents, reagents, glassware, plastic-ware, syringes, SPE cartridges, and laboratory instrumentation.[198,270,271] Contamination has even been traced to cement holding needles to syringes.[198,270] Ways to overcome and reduce BPA background levels include Empore (polystyrene-divinylbenzene disk) filtration, baking glassware at high temperatures (> 400°C), and solvent washing steps.[198,226,271,272] Procedural blanks during preparation and analysis can help to pinpoint contamination sources.[198]

Common sample preparation techniques for BPA include liquid-liquid extraction (LLE), solid phase extraction (SPE), and solid phase microextraction (SPME). The range of extraction solvents for BPA LLE include acetonitrile[273], dichloromethane[196,274-278], ethyl acetate[144,279], heptane[273], and trichloromethane[280]. SPE has largely replaced LLE due to environmental concerns over large solvent volume usage. Non-selective SPE sorbents are summarized in Table 1.6 and the elution solvents for BPA include acetone[281,282], acetone/methanol[197], acetonitrile[93], acetonitrile/water[283], chloroform[154], dichloromethane[196], dichloromethane/hexane[97,284], dichloromethane/methanol[284], diethyl ether/methanol[99], ethyl acetate[101,279,282,285-287], ethyl acetate/methanol[288], methanol[166,282,289-292], methanol/water[143], and propanol/ methyl tert-butyl ether (MTBE)[293]. SPME fiber polymer materials that have been used in the extraction of BPA include CAR/PDMS[294], CW[295], CW/DVB[294,296], PA[281,294-296], PDMS[281,294-296], and PDMS/DVB[281,294,295]. Other preparative techniques that have been used with BPA include hollow fiber liquid-liquid-liquid microextraction (HF-LLLME)[297], micro liquid-liquid extraction (MLLE)[298],

Table 1.6 Solid phase extraction (SPE) cartridge sorbent materials for bisphenol A sample preparation.

Sorbent	Phase	Cartridge	Reference
C8 chains (silica-based)	reverse phase	Varian C8	154,
C18 chains (silica-based)	reverse phase	Alltech™ Maxi-Clean™ C18 Baker C18 Biotage Isolute® C18 Biotage Isolute® C18/ENV+ Merck Millipore LiChrolut® RP-18 Supelco DSC-18 Varian Bond Elute C18 Waters Sep-Pak C18 Waters Sep-Pak Classic C18 Waters Sep-Pak Plus C18	97, 143, 147, 153, 279, 281, 282, 289, 291, 292, 299
C18 chains with sulfonic acid ($-SO3^-$) and quaternary amine ($-NR_3^+$) groups	reverse phase	Biotage Isolute® Multimode	283
hydroxylated PS-DVB	reverse phase	Biotage Isolute® ENV+	99
PS-DVB	reverse phase	3M™ SDB-XC Baker PS-DVB Hamilton PRP-1 Merck Millipore LiChrolut® EN	93, 99, 191, 279, 281, 300
poly(divinylbenzene-*co*-*N*-vinylpyrrolidone	reverse phase	Phenomenex Strata™-X Waters Oasis® HLB	99, 101, 143, 153, 166, 194, 196, 197, 215, 282, 285-288, 290, 293
polyamide resin	reverse phase	Supelco Discovery® DPA-6S	282

PS-DVB = polystyrene-divinylbenzene

vortex assisted-LLME (VA-LLME)[301], vesicular coacervative extraction[302], non-ionic surfactant extraction[303], adsorption on supported ionic liquid membranes (SILMs)[304], continuous flow liquid membrane extraction (CF-LME)[305], extraction with molecularly imprinted polymers[306,307], magnetic carbon nanotube SPE[308], and stir bar sorptive extraction (SBSE)[309,310].

GC/MS and LC/MS are frequently used in the detection of BPA. A limitation of GC/MS is that analytes must be volatile and converted to the gas phase. While BPA is volatile, the hydroxyl groups hinder volatilization, so they are often derivatized to provide better volatilization and lower detection limits. Derivatization through the silylation of BPA changes the hydroxyl groups to trimethylsilyl groups which are more amenable to transfer into the gas phase. Common silylation reagents include N,O-bis(trimethylsilyl) acetamide (BSA)+chloroform[280], N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA)[196,276,284], BSTFA+dichloromethane[311], BSTFA+pyridine[97,101,286], BSTFA+trimethylchlorosilane (TMCS)[99,191,287], BSTFA (1% TMCS)+pyridine[277,282,287], N-Methyl-N-tert-butyldimethylsilyltrifluoroacetamide (MTBSTFA)[279], and TMSC+hexamethyldisilazane (HMDS)+pyridine[275]. Acylation with acetic anhydride can also be used for BPA derivatization and converts hydroxyl groups to esters.[273]

The GC columns used for BPA are composed of (5%-phenyl)-methylpolysiloxane[97,99,101,154,191,196,273,278,279,281,282,284-288,294,311,312], 100% dimethyl polysiloxane[153,274,275,277,280], or (35% phenyl)-methylpolysiloxane[276]. Electron ionization (EI)[99,101,274-277,280-282,285,287,288,311] is the MS ionization mechanism and can be operated in scan[97,279,282,284,285,287,311,313] or SIM[97,99,101,154,191,196,273-277,280-282,285,288,294,296,311,312] modes. Other configurations that have been used for BPA analysis include quadrupole ion traps with MS/MS

instruments[99,101,281,282,284-286], APGC(atmospheric pressure GC)–ToF-MS[309], isotope dilution GC/MS[314], and GC/FID[278,299].

LC/MS has become popular in recent years due to less sample preparation. For example, BPA can be injected in aqueous solution, whereas GC injection requires extraction to an organic solvent phase and derivatization. Columns employed for BPA include reverse phase alkyl amides[194], C8[300], C18[142-144,147,153,197,215,266,283,289-291,293,295,313,315-317], and porous graphitic carbon[154]. Gradient elution composition varies and includes 0.1% acetic acid and ammonium acetate/ACN (50% MeOH)[194], 0.5 to 1% acetic acid or formic acid/ACN[93,215,300], water/ACN (50% MeOH)[317], 1 mM ammonium formate (20% ACN)/ACN[293], water/ACN[290], water (50% ACN)/ACN[313], water/MeOH[142,166,289], and water (20% MeOH)/MeOH[143,197,291]; isocratic elution options include ACN[316], water/ACN[153,147,283,295], and water/MeOH[154]. Two common MS ionization techniques for BPA are APCI[143, 197,289-291,293] and ESI[93,142,143,197,215,290,293,317,318]. ESI is easily coupled to LC systems since it ionizes analytes eluting from the LC column. Limitations of ESI are that the ionization is variable and influenced by many factors, including the sample matrix.[319] Due to this variability there is no spectral library. On the other hand, GC EI is highly reproducible, with a spectral library for identification of unknowns. Tandem quadrupole and quadrupole ion trap mass analyzers are frequently used for BPA detection since they provide detailed information through MS/MS[142,215,289,317,318] (scans[93,291,318] and MRM[143,179,194,197,290,293,318]) and MS^n experiments[289].

Tandem-in-space triple quadrupole mass spectrometers are advantageous for environmental sample analysis since their low-level detection and multiple scan modes provide a wealth of information. These tandem-in-space configurations have two quadrupoles (Q1 and

Q3) that provide mass selection and one quadrupole (q2) that enables collision induced dissociation (Figure 1.9).[319] The ion undergoing fragmentation is referred to as the precursor ion (or parent ion in older nomenclature) and the product ion (or daughter ion in older nomenclature) is the ion resulting from the dissociation of the precursor ion.[319] Several scan modes are possible and each provides information by scanning or selecting specific ions (Figure 1.9). The product ion scan provides data about all product ions that have fragmented from a specific precursor ion. Precursor ion scan provides information about all the starting precursor ions that give a specific product ion. A neutral loss scan provides information about products that have lost a neutral fragment during dissociation. The final scan mode is SIM or MRM and selects a specific precursor and product ion (no scanning). MRM is very useful when monitoring BPA in samples because it provides very specific detection.

Other methods for BPA detection include electrochemical techniques[320-326], quantum dot amperometric sensor [327], LC-UV, and LC- fluorescence detection (FD). These detection limits tend to be higher when compared to MS and are not used frequently in low-level BPA detection. BPA detection by UV is done between 228nm[153] and 280nm[144,313]. For FD detection, BPA is excited at 225 to 275 nm and emits fluorescence at 295 to 317 nm.[147,154,266,283,295] Various fluorescence derivatizations have been done with BPA[316,328] and fluorescent probes[329,330].

For other structurally similar bisphenol compounds (BPB, BPE, BPF, and BPS) and for halogenated (chlorinated) BPA by-products, the LC/MS and GC/MS techniques described for BPA can be used.[142,147,179,215,273,289,280,317,311] Bisphenol diglycidyl ethers (BDGEs) require a slight modification to LC conditions with the addition of ammonia to the mobile phase to enhance ionization.[166] The ESI mechanism is slightly different; the BDGE ions are detected as adducts

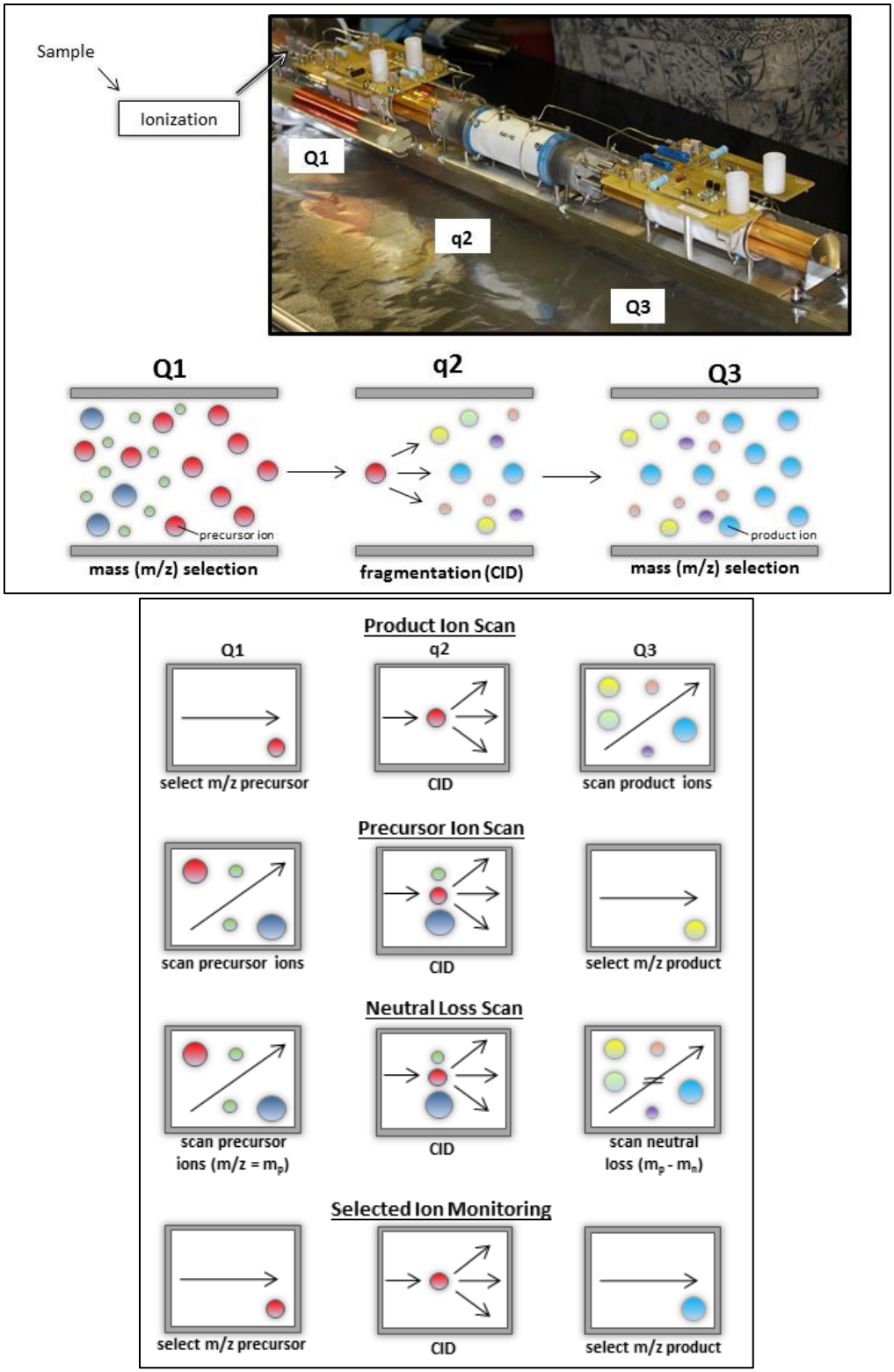


Figure 1.9 Tandem-in-space triple quadrupole mass spectrometer and ion scan modes. The first and third quadrupole (Q1 and Q3) provide mass (m/z) selection and collision induced dissociation (CID) occurs in the second quadrupole (q2).

(whereas just the ion is detected for BPA and related compounds).[166] Similar LC/FD[147,172,266,295,331], LC/FD[313], LC/MS[172,166], and GC/MS[172,280,296,313] methods for BPA have also been used in BDGE analyses.

1.4 Research Objectives

In the last several years there has been increasing interest in using pipe lining and coating technologies in drinking water service lines to prevent pipe corrosion and leaching of metals. This has created a need for information about the technologies such that water utilities, engineering consultants, state regulators, and consumers can make well-informed decisions. The EPA provided a research grant to the Water Research Foundation to comprehensively evaluate lining and coating technologies and provide information about the available technologies, costs, ability to stop metal leaching, and the leaching of organic compounds (constituents). This project was funded under the Water Research Foundation grant and has identified epoxy coatings and PET liners as two of the most promising and commercially available technologies for use in small diameter drinking water service lines.

This dissertation research addresses the leaching of organic compounds from an epoxy coating and a PET liner. The main objectives were to develop analytical methods for identification of key organic leachates and determine key leachate reactions in drinking water. Key organic leachates are those commonly associated with the coating or lining material: bisphenols and BDGEs were the analytes of focus for the epoxy coating (Table 1.4 and Figure 1.7) and phthalates (Table 1.2 and Figure 1.5) for the PET liner. The reactions studied were limited to those likely to occur in drinking water: hydrolysis and chlorination. Phthalates were

not investigated for hydrolysis or chlorination because their chemical structures are not favorable for those reactions (Section 1.2.1).

The specific aims of analytical method development were to develop LC/MS/MS methods for bisphenols and BDGEs, develop LC/MS or GC/MS methods for phthalates and phthalic acids, eliminate potential contamination sources, and apply the analytical methods during fill-and-dump pipe studies. The analytical methods needed to be provide low-level (µg/L) detection such that the analytes could be detected at concentrations relevant to regulated levels. Since significant background levels of the key analytes are often reported in laboratory settings due to their presence in commonly used materials (Sections 1.2.3 and 1.3.3), elimination or reduction of background contamination was important in preventing false positives.

The specific aims for the determination of reactivity in drinking water were to investigate the hydrolysis of the key analytes (BPA, BPF, BADGE, and BFDGE), to study the chlorination of the key analytes with free chlorine and monochloramine, to develop kinetic models to predict analyte concentrations after hydrolysis or chlorination, and to monitor the formation of key hydrolysis and chlorination by-products (Figures 1.6 and 1.7). BPA and BPF were chosen as representative bisphenols because they are the two bisphenol compounds most frequently used in epoxy coatings and also most frequently reported in the aquatic environment (Section 1.3). BADGE and BFDGE were investigated because they are the reactive epoxy prepolymers corresponding to BPA and BPF. Development of kinetic models provides tools that can be used during risk assessments (by others) to estimate analyte concentrations in drinking water under a broad range of conditions. Assessments of drinking water safety require

more than just identification of leached compounds; they also require an understanding of the rate at which these compounds are transformed and identification of the resulting by-products. These transformations may increase or decrease toxicity, which may require changes in regulations.

These research objectives are addressed in the chapters to follow. Chapter 2 describes optimization of the LC/MS/MS and GC/MS and methods used to identify and quantify key leachates (i.e., bisphenols, BDGEs, phthalates, and phthalic acids), along with preliminary chlorination studies, and the fill-and-dump experiments used to detect leaching of organic contaminants from epoxy-coated and PET-lined sections of lead and copper service lines. Chapter 3 elucidates unexpected leachates discovered during epoxy coating fill-and-dump testing. Chapter 4 is an investigation into hydrolysis of the key analytes (BPA, BADGE, and BFDGE) and includes the development of a kinetic hydrolysis model. Chapter 5 examines the reactivity of key analytes (BPA, BPF, and BADGE) with chlorine (free chlorine and monochloramine) and includes the development of a kinetic model describing chlorination of BPA and BPF under drinking water conditions.

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Chapter 2: Organic Leachates from an Epoxy Coating and a PET Liner

2.1 Introduction

Service lines are used in drinking water distribution systems to transport water from the main to a building or private residence. These pipes, if made from lead or copper, are respectively termed lead service lines (LSL) and copper service lines (CSL). Pipe corrosion can cause leaching of lead and copper into the water supply. The 1988 amendment to the Safe Drinking Water Act, The Lead Contamination Control Act (LCCA), prohibited the use of lead service lines (LSLs) and limited the use of lead-containing products in drinking water distribution systems.[1,2] LSLs in place before 1988 could remain in use and in 1990 there were an estimated 3.3 million LSLs in the U.S.[3]

To address health concerns about leached metals, the Environmental Protection Agency's (EPA) Lead and Copper Rule (LCR) regulates the amount of lead and copper in drinking water. Action levels have been established and if the concentration in the drinking water exceeds the level in 10% of field samples, a utility must take steps to lower it.[4] The action level is 15 ppb (parts-per-billon or μg/L) for lead and 1,300 ppb for copper.[4] Lead is especially concerning because at levels above the action limit it causes problems in childhood mental and physical development, and prolonged exposure in adults is believed to cause high blood pressure and kidney problems.[5] Copper exposure above the action level can cause gastrointestinal distress and long-term exposure has been associated with liver and kidney damage.[6]

Under the LCR, the steps a utility can take to lower lead levels include corrosion control methods and, usually as a final step, pipe replacement.[7] Pipe replacement options include

partial LSL replacement and full LSL replacement; partial replacement replaces the portion of service line owned by the utility, while full replacement replaces the service line owned by the utility and the homeowner. [8] However, replacement can be costly, time-consuming, and damaging to the property. In a District of Columbia (DC) LSL replacement program, implemented after an EPA mandate[9], higher levels of lead were observed for months after partial LSL replacement due to disturbance of the portions of the LSLs that were not replaced[10,11]. Alternative methods are being sought to eliminate the need to physically remove the pipe. One such alternative technology is placement of a lining or coating inside the pipe to prevent or reduce leaching of metals.

Two such technologies being considered by utilities in the U.S. and being employed in various locations elsewhere are epoxy coatings and polyethylene terephthalate (PET) liners. While these technologies eliminate the need for pipe removal there is concern that linings or coatings may leach organics into the drinking water. The formation of PET plastic involves the reaction of terephthalic acid (TPA) with ethylene glycol to form a polymerized plastic.[12] The PET slip liner is inserted into the aging pipe and then expanded to form a close fit with the pipe.[3] Potential leachates from PET include phthalic acids (PAs)[13,14] and phthalate esters (PAEs)[13-18], with leached levels depending on the purity of the PET.[19]

Potable water grade epoxy coatings are prepared from two starting materials: a prepolymer and a hardener. The prepolymer is commonly prepared by partially polymerizing a bisphenol diglycidyl ether (BDGE), such as bisphenol A diglycidyl ether (BADGE) or bisphenol F diglycidyl ether (BFDGE) with an epichlorohydrin (Figure 2.1). BADGE and BFDGE are the polymerically active form of bisphenol A (BPA) and bisphenol F (BPF). The hardener is often a

polymeric amine, such as triethylenetetramine (TETA).[20] The two components are mixed, applied to the pipe, and allowed to cure.[21] BPA has been reported leaching from epoxy coatings into drinking water[22,23] and BADGE has been found to leach from epoxy can coatings into foods[24]. There has been significant negative media attention surrounding BPA and manufacturers are considering switching to structurally similar bisphenols: bisphenol B, D, E, F, S (BPB, BPD, BPE, BPF, BPS; Figure 2.1).[25,26] BPF has been reported leaching from potable water grade epoxy[22] and BFDGE into canned foods[27].

BPA is an endocrine disrupting chemical correlated (causation not proven) with negative impacts on reproduction, neurobehavioral development, and metabolic diseases (e.g. obesity, diabetes, heart disease, thyroid and liver function).[28] The harm of low-level chronic exposure to BPA is currently debated in the scientific community.[29] The U.S. Environmental Protection Agency (EPA) and U.S. Food and Drug Administration (FDA) have chosen not to regulate BPA nor is it included in EPA's third drinking water candidate contaminant list (CCL3) or fourth list (CCL4).[30-32] The other bisphenols being considered as replacements for BPA have similar estrogenic activity[33,34] and are also unregulated by the EPA and FDA. The National Sanitation Foundation (NSF) recommends a BPA drinking water criterion of 0.1 mg/L total allowable concentration and 0.01 mg/L single-product allowable concentration.[35]

An additional consideration for drinking water risk assessments is the stability of the contaminants once they have leached into the water. Drinking water is often disinfected with chlorine and there are known chlorination products of BPA and BDGEs: BPA-Cl, BPA-2Cl, BPA-3Cl, BPA-4Cl, BADGE-HCl, BADGE-2HCl, BADGE-H_2O-HCl, BFDGE-HCl, BFDGE-2HCl, and BFDGE-H_2O-HCl (Figure 2.2). Chlorinated by-products have been detected in drinking water treatment

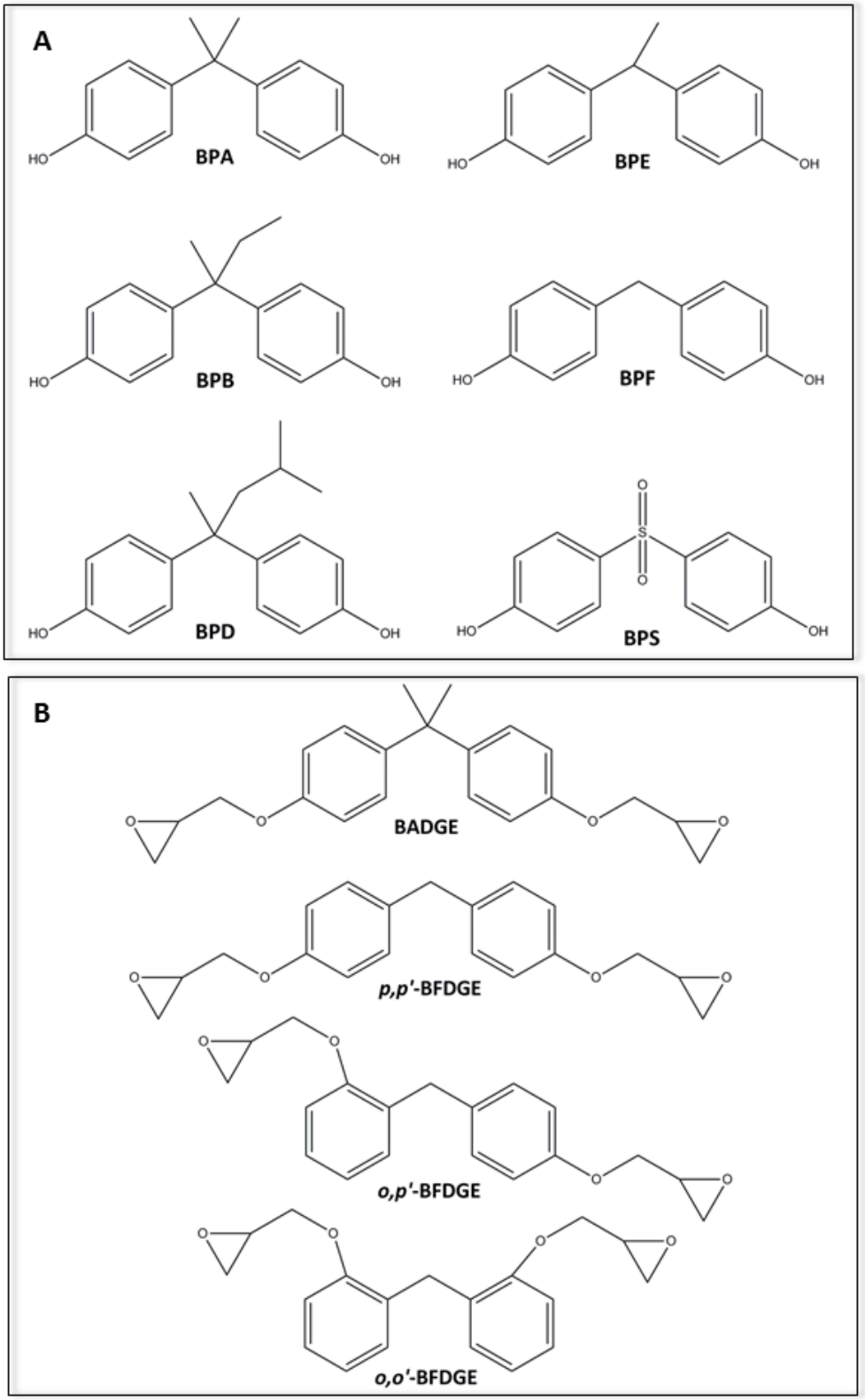


Figure 2.1 Potential organic leachates from epoxy coatings: bisphenols (A) and bisphenol diglycidyl ethers (B).

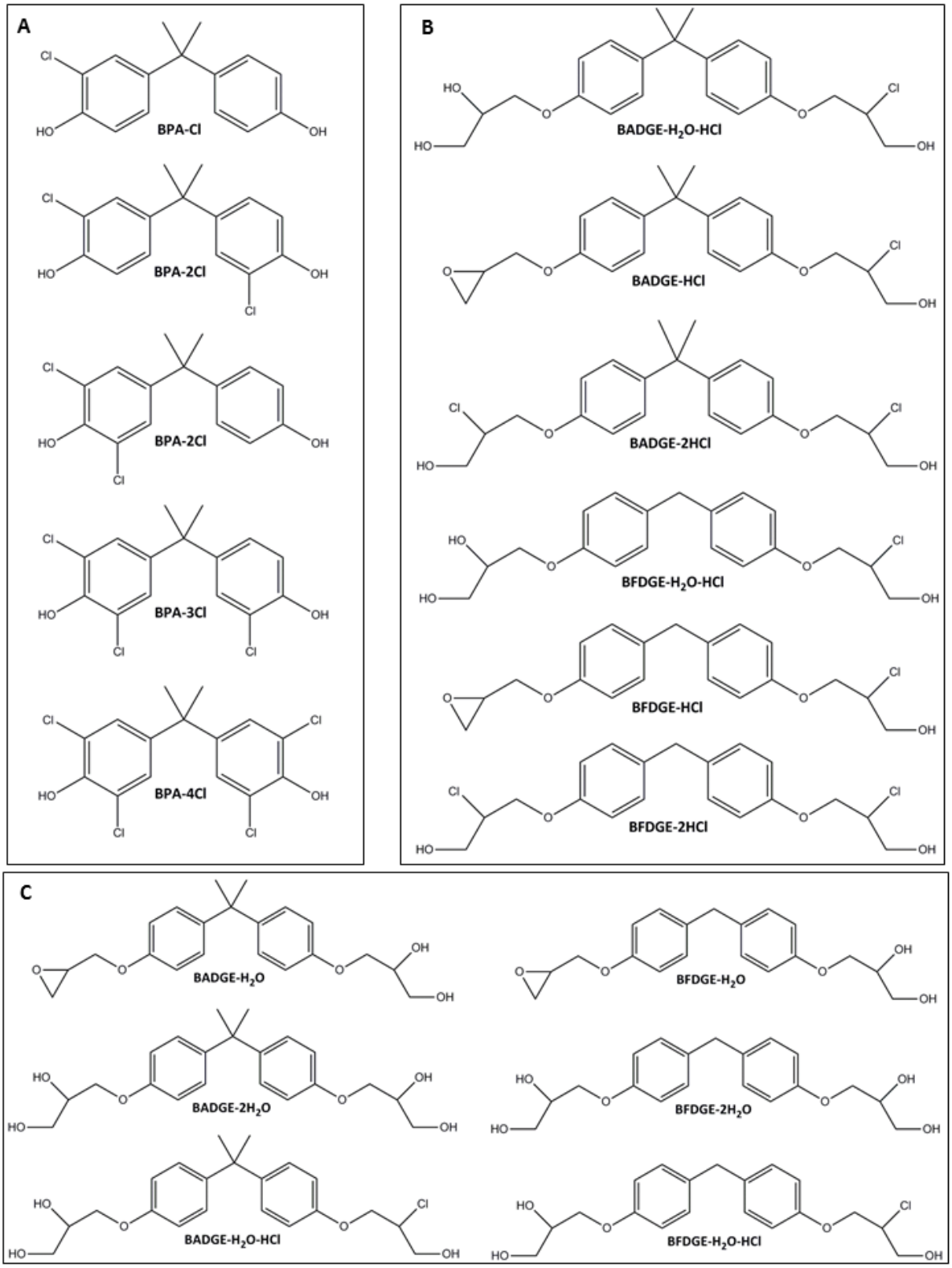


Figure 2.2 Key compounds associated with drinking water reactions: (A) chlorinated bisphenol A by-products, (B) chlorinated bisphenols diglycidyl ether by-products, and (C) bisphenols diglycidyl ether hydrolysis by-products.

facilities[36,37], drinking water[38], and in water samples collected from epoxy-coated drinking water pipes[23]. Chlorination of compounds leads to concerns about changes in their toxicity; for example, BPA-Cl and BPA-2Cl have a higher human α-estrogen receptor affinity (greater estrogenic activity).[39] There are also hydrolysis products of BDGEs (BADGE-H_2O, BADGE-$2H_2O$, BADGE-H_2O-HCl, BFDGE-H_2O, BFDGE-$2H_2O$, and BFDGE-H_2O-HCl; Figure 2.2).[40-43] These by-products are not regulated in the U.S. but the European Union has a 9 mg/kg food migration limit for BADGE and its hydrolysis products and a 1 mg/kg food migration limit for the chlorinated BADGE by-products.[44]

The main methods for low-level detection of bisphenols, BDGEs, PAs, and PAEs are GC/MS and LC/MS.[45,46] Analytically, the challenge in measuring BPA and phthalates is preventing background levels and sample contamination. BPA and phthalates are ubiquitously present in the laboratory environment making low-level analytical detection challenging.[46,47] Everything that comes into contact with the sample must be evaluated to avoid contamination and false positives.

This chapter addresses the leaching of organic compounds from an epoxy coating and a PET liner. The epoxy and PET liner were selected because they were deemed to be representative of the most promising and commercially available technologies for use in small diameter drinking water service lines. The main objectives were to develop analytical methods for identification of key organic leachates and determine leachate reactivity with water and chlorine. The key organic leachates were selected from among compounds in the starting materials that may leach into water or form by-products in concentrations high enough to be of public health or regulatory concern. For the epoxy coating, bisphenols and BDGEs were

determined to be the key leachates (Figures 2.1 and 2.2), and phthalates (phthalates esters and phthalic acids) were the key leachates of focus for the PET liner. The specific aims for analytical method development were to develop LC/MS/MS methods for bisphenols and BDGEs, develop LC/MS or GC/MS methods for phthalate esters and phthalic acids, eliminate potential contamination sources, obtain low-level (μg/L) method detection limits, and apply the analytical methods during fill-and-dump pipe studies. One part of the fill-and-dump pipe studies consisted of filling the pipe sections with chlorinated extraction water. For this reason, a preliminary investigation of chlorine reactivity was done with key bisphenols and BDGEs Phthalates were not investigated for chlorination since their chemical structures are not favorable for those reactions. Chlorination will be explored in greater depth in Chapter 5.

2.2 Materials and Methods

2.2.1 Chemicals and Reagents

Water used during LC/MS analyte optimization was Optima LC/MS grade water from Fisher Scientific (Pittsburgh, PA). After optimization, water for LC/MS instrumentation was prepared using a Millipore Elix Reverse Osmosis system followed by a Millipore A10 unit and is referred to as reagent water herein. The reagent was water found to be equivalent to the Fisher Optima LC/MS grade water. Tap water was collected after the tap was allowed to run for 5 min, thereby reducing the concentration of any contaminants contributed by the faucet and by smaller water pipes within the building.

LSLs approximately 100 years old and recently removed from service were cut into sections 3.5 to 4.0 ft. long and sent to the University of Kansas by the Rochester (New York) Water Bureau. Pipe sections with inner diameters (IDs) of both 0.50 and 0.625 (5/8) in. were

sent, but most had an ID of 0.625 in. and only these were used in the experiments reported herein. Four-foot long CSL sections were cut from a 50 ft. roll of Type L potable water grade 'soft' annealed copper tubing (ASTM B-88, Great Lakes Copper Inc., London, Ontario, Canada) with a nominal size of 0.625 (5/8) in. and an actual ID slightly larger than 5/8 in.

A two-part (part A and B) potable-water-grade epoxy resin was applied by the manufacturer to both the LSL and CSL pipe sections, ensuring proper application and curing time. Part A was the epoxy resin, or prepolymer (subsequently determined to be BADGE based) and part B was the polyfunctional amine hardener (containing TETA). An NSF-61-G[48] certified PET (polyethylene terephthalate) liner was applied by the manufacturer to a second set of LSL and CSL pipe sections.

Supplies for chlorine analysis (Hach accuvac vials and monochloramine reagents) and nitrogen analysis (free ammonia reagents) were purchased from the Hach Company (Loveland, CO). Stock hypochlorous acid (free chlorine) and monochloramine solutions were prepared using laboratory-grade sodium hypochlorite solution and ACS reagent-grade ammonium chloride which were purchased from Fisher Scientific (Pittsburgh, PA).

Syringe filters investigated for use with bisphenols were: Fisherbrand™ sterile mixed cellulose ester (MCE) membrane (0.22 µm pore size, 25 mm diameter) syringe filters and Fisherbrand™ nonsterile nylon membrane (0.45 µm pore size, 33 mm diameter) syringe filters purchased from Fisher Scientific (Pittsburgh, PA); Microliter polytetrafluoroethylene (PFTE) membrane (0.45 µm pore size, 25 mm diameter) syringe filters from Wheaton (Millville, NJ); and Nuclepore nonsterile polycarbonate (0.40 µm, 13 mm diameter) filters from Nuclepore Corporation (Pleasanton, CA).

HPLC grade acetonitrile , HPLC grade chloroform, HPLC grade hexanes, LC/MS grade methanol (Optima), hydrochloric acid, calcium chloride, monobasic and dibasic sodium phosphate, sodium bicarbonate, sodium bisulfite, sodium chloride, sodium hydroxide, and the chlorine quenching agents 99% L-ascorbic acid sodium salt, sodium bisulfite, sodium thiosulfate, and sodium sulfite were purchased from Fisher Scientific (Pittsburgh, PA). Ammonium formate, formic acid, and trichlorophenol were purchased from Sigma Aldrich (St. Louis, MO). All chemicals were ACS reagent-grade unless otherwise specified.

Bisphenols (i.e., BPA, BPB, BPD, BPE), were purchased from TCI America (Portland, OR), BPF and the deuterated internal standard (BPA-D16) from Sigma Aldrich (St. Louis, MO), and the deuterated surrogate internal standard (BPA-D8) from Cambridge Isotopes Laboratory (Tewksbury, MA). Chlorinated bisphenol A standards (BPA-Cl, BPA-2Cl, BPA-3Cl) were purchased from Santa Cruz Biotechnology (Dallas, TX) and BPA-4Cl from TCI America (Portland, OR). Diglycidyl ether compounds (BADGE, BADGE-H_2O, BADGE-$2H_2O$, BADGE-H_2O-HCl, BADGE-HCl, BADGE-2HCl) were purchased from Sigma Aldrich (St. Louis, MO), BFDGE from Crescent Chemical Co. (Islandia, NY), and the deuterated internal standard sulfamethoxazole-D4 (SMXL-D4) from Toronto Research Company (Toronto, Ontario, Canada).

The following phthalate esters were ordered from Fisher Scientific (Pittsburgh, PA): 99% di-n-butyl phthalate (DNBP) (Acros Organics), 99% diethyl phthalate (DEP) (Acros Organics), 98% diethyl hexyl phthalate (DEHP) (Acros Organics), 97% butyl benzyl phthalate (BBP) (Acros Organics), 99% dimethyl phthalate (DMP) (Acros Organics), 99% Dimethyl isophthalate (DMIP) (Acros Organics), 99% dimethyl terephthalate (DMTP) (Acros Organics), 99% bis(2-ethylhexyl) adipate (DEHA) (Acros Organics), 98% di-n-octyl phthalate (DNOP) (Alfa Aesar), and 95% diethyl

terephthalate (DETP) (Alfa Aesar). One phthalate, 95(+)% diethyl phthalate (DEP), was ordered from Ultra Scientific (North Kingstown, RI). The deuterated surrogate internal standard dihexyl phthalate-D4 (DNHP-D4) and deuterated internal standard phenanthrene-D10 (PANE-D10) were ordered from Sigma Aldrich (St. Louis, MO). The phthalic acids, 99% phthalic acid (PA), 99% isophthalic acid (IPA), and >99% terephthalic acid (TPA), were ordered from Fisher Scientific (Pittsburgh, PA).

2.2.2 Instrumental Methods of Analysis

2.2.2.1 LC/MS/MS Analysis of Bisphenols

The liquid chromatography/triple quadruple mass spectrometry (LC/MS/MS) method for bisphenols was adapted from a previously described method.[25] The LC/MS system consisted of a Shimadzu (Columbia, MD) Prominence High Performance LC (HPLC) equipped with a LC-20AB binary pump, DGU-20A3 degasser, and SIL-20A autosampler coupled to a 4000 QTrap triple-quadrupole linear ion-trap mass spectrometer with a turbo ion-spray source (AB SciEx, Framingham, MA). A Gemini-NX C18-with-TMS-endcapping column (Phenomenex, Torrance, CA), 150 × 3.0 mm, 3-micron particle size was selected such that reverse phase chromatographic separation could be achieved over a broad pH range (2 to 12). A 50 µL aliquot of sample was injected and carried by a water and methanol mobile phase at a flow rate of 0.4 mL/min. The gradient mobile phase was applied with the following percentage of methanol: held at 65% for 1 min, ramped from 65% to 85% over 5 min, held at 85% for 6 min, ramped from 85% to 100% over 3 min, held at 100% for 2 min, then returned to 65% over 4 min and held for 5 min.

The MS electrospray source was operated with nitrogen gas for nebulization. The MS/MS parameters were optimized for each analyte and are summarized in Table 2.1. Samples from pipe sections were filtered using syringe filters conditioned with reagent water prior to use. BPA-D8 was used as the surrogate internal standard (to provide correction for filter losses and instrumental variation) and BPA-D16 was used as the internal standard (to provide corrections for instrumental variation). A linear calibration curve was used for quantitation and the method detection limits (MDL) were determined as described in *Standard Methods* Method 1030C, Method Detection Limit[49]. Additionally the signal-to-noise (S/N) value was always kept above 2; anything below 2 was considered noise[50] (refer to the standard operating procedure (SOP) in Appendix section A.1.4 for additional details). Examples of chromatograms with elution times and calibration curves used for quantitation are shown in Figure 2.3.

2.2.2.3 LC/MS/MS Analysis of Bisphenol Diglycidyl Ethers (BDGEs)

The LC/MS/MS method for BDGEs was adapted from a previously described method[42] and the instrumental system described for the bisphenols was also used for the BDGEs. A Gemini-NX C18-with-TMS-endcapping column(Phenomenex, Torrance, CA), 150 × 3.0 mm, 3-micron particle size was selected such that reverse phase chromatographic separation could be achieved with samples in the pH range of 2 to 12. A 50 µL aliquot of sample was injected at a flow rate of 0.4 mL/min. The gradient mobile phase was ammonium formate at pH 3.75 and methanol. The gradient used was 30% to 60% methanol over 4.5 min, then from 60% to 84% methanol over 5 min, from 84% to 90% methanol over 10 min, from 90% to 100% methanol over 5 min, held at 100% methanol for 2 min, and then returned to 60% methanol over 5 min.

The MS electrospray source was operated with nitrogen gas for nebulization. The ammonium in the mobile phase was present to facilitate the formation of a BDGE adduct. The BDGE ion is not stable in the electrospray but the BDGE ammonium adducts are stable. The MS/MS parameters were optimized for each analyte and are summarized, with MDLs, in Table 2.2. Because BADGE is susceptible to hydrolysis, calibration standards and run standards were prepared every 24 hours and all samples were run within 24 hours of sampling. SMXL-D4 was selected as the internal standard because a deuterated BDGE was not commercially available. The BDGE response was linear from 0 to 200 µg/L and non-linear from 200 µg/L and above (Figure 2.4). To avoid the use of a non-linear polynomial calibration curve, samples were diluted to within the range of the linear calibration curve.

2.2.2.4 GC/MS Analysis of Bisphenols and BADGE in Epoxy

Gas chromatography mass spectrometry (GC/MS) was used to determine key starting materials in the epoxy resin. Due to reactivity of the epoxy starting materials (part A and part B) GC/MS was selected to prevent contamination and epoxy coating of the LC/MS system. An Agilent (Agilent Technologies, Santa Clara, CA) 6890A GC with Agilent 5973N MS 7683 autosampler and HP-5MS 0.25 mm ID x 30 m column with a 0.25-µm film thickness was operated in scan mode from 40 to 550 Da. Helium was used as the carrier gas and the transfer line temperature was 270°C. The sample solvent was methanol (with a 3.5 min solvent delay), and a 1.0 µL splitless injection was made at an injection temperature of 270°C with a constant carrier gas flow rate of 1.0 mL/ min. The oven temperature was held at 100°C for 0.5 min then ramped at 9°C/min to 300°C. Standards of bisphenols and BADGE were run prior to any MS scans to confirm the analytes' detection.

Table 2.1 MS parameters for the LC/MS/MS analysis of bisphenols and chlorinated by-products.

Compound	CAS Number	Precursor Ion (m/z)		Product Ion (m/z)	DP (V)	CE (V)	CXP (V)	MDL (µg/L)
BPA	80-05-7	**$[M-H]^-$**	**227.0**	**212.0**	-76.02	-24.87	-3.12	0.057
		$[M-H]^-$	227.0	133.0	-76.02	-31.26	-10.35	
BPA-Cl	74192-35-1	**$[M-H]^-$**	**261.7**	**181.9**	-69.59	-41.39	-12.97	13.6
		$[M-H]^-$	261.7	245.8	-44.96	-29.12	-14.74	
BPA-2Cl	79-98-1	**$[M-H]^-$**	**295.0**	**243.8**	-84.88	-32.91	-5.10	1.8
		$[M-H]^-$	295.0	216.1	-49.95	-41.35	-32.37	
BPA-3Cl	40346-55-2	**$[M-H]^-$**	**330.6**	**252.0**	-40.15	-44.21	-8.36	3.2
		$[M-H]^-$	330.6	278.0	-52.96	-35.24	-12.26	
BPA-4Cl	79-95-8	**$[M-H]^-$**	**365.0**	**314.0**	-81.19	-35.77	-13.06	5.9
		$[M-H]^-$	365.0	286.0	-33.04	-45.66	-13.26	
BPB	77-40-7	**$[M-H]^-$**	**241.0**	**212.0**	-66.98	-24.20	-9.44	0.18
		$[M-H]^-$	241.0	211.0	-66.98	-34.76	-13.10	
BPD	6807-17-6	**$[M-H]^-$**	**269.0**	**212.0**	-82.07	-25.08	-16.67	0.1
		$[M-H]^-$	269.0	211.0	-82.07	-35.56	-3.60	
BPE	2081-08-5	**$[M-H]^-$**	**213.0**	**198.0**	-68.21	-23.37	-3.02	0.07
		$[M-H]^-$	213.0	199.0	-68.21	-37.54	-3.44	
BPF	620-92-8	**$[M-H]^-$**	**199.0**	**93.0**	-67.19	-29.07	-6.88	0.18
		$[M-H]^-$	199.0	105.0	-70.68	-28.42	-5.56	
BPA-D8	92739-58-7	**$[M-H]^-$**	**235.0**	**220.0**	-76.20	-25.68	-4.58	NA
		$[M-H]^-$	235.0	137.0	-78.04	-35.62	-8.86	
BPA-D16	96210-87-6	**$[M-H]^-$**	**241.0**	**142.0**	-84.38	-37.51	-10.54	NA
		$[M-H]^-$	241.0	222.0	-71.80	-40.84	-15.26	
TCP	88-06-2	**$[M-H]^-$**	**194.7**	**35.0**	-29.98	-44.79	-3.50	NA
		$[M-H]^-$	194.7	158.8	-64.45	-29.97	-24.66	

transitions in bold are quantitation ions NA = Not applicable

DP = Declustering potential CE = Collision energy CXP = Collision cell exit potential

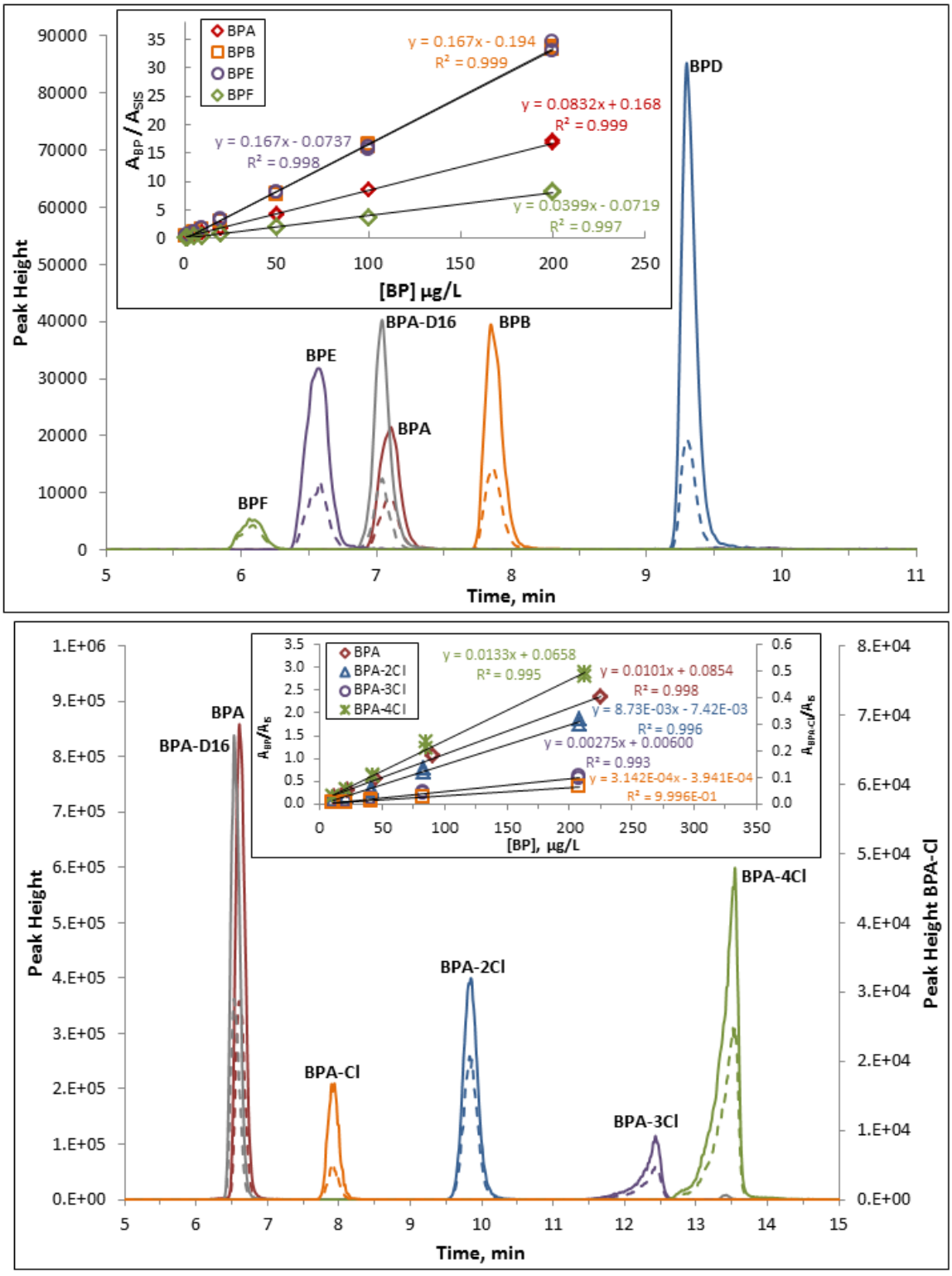


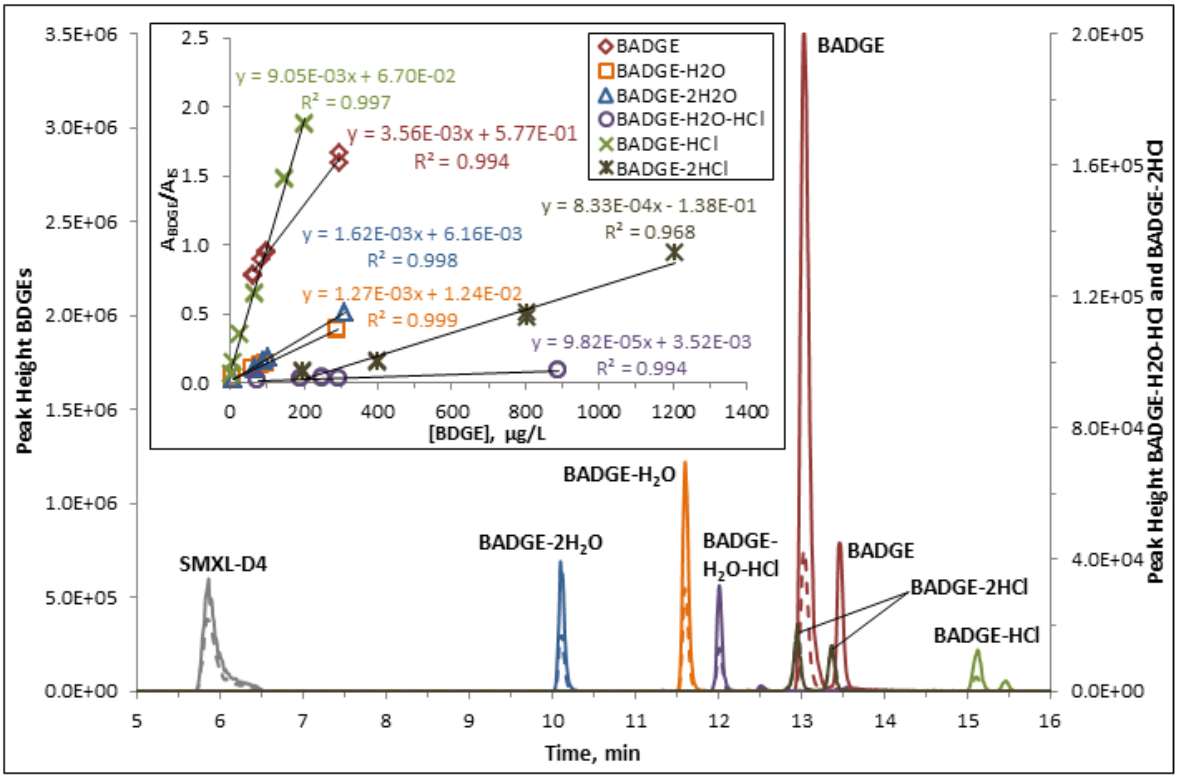
Figure 2.3 LC/MS/MS chromatogram of a 20 µg/L mixed bisphenols standard and calibration curves (top). LC/MS/MS chromatogram of an 80 µg/L mixed chlorinated bisphenol A standard and calibration curves (bottom).

Table 2.2 MS parameters for the LC/MS/MS analysis of bisphenol diglycidyl ethers.

Compound	CAS Number	Precursor Ion (m/z)		Product Ion (m/z)	DP (V)	CE (V)	CXP (V)	MDL (µg/L)
BADGE	1675-54-3	**$[M+NH4]^+$**	**358.2**	**191.0**	51.95	21.49	12.04	7.00
		$[M+NH4]^+$	358.2	135.0	51.95	43.41	7.61	
BADGE-H_2O	76002-91-0	**$[M+NH4]^+$**	**376.4**	**209.0**	46.49	20.47	12.37	1.50
		$[M+NH4]^+$	376.4	135.0	46.49	40.38	6.46	
BADGE-$2H_2O$	5581-32-8	**$[M+NH4]^+$**	**394.4**	**209.0**	46.87	23.71	12.24	1.40
		$[M+NH4]^+$	394.4	135.0	46.87	46.16	6.32	
BADGE-H_2O-HCl	227947-06-0	**$[M+NH4]^+$**	**412.8**	**135.0**	38.50	48.57	6.11	7.60
		$[M+NH4]^+$	412.8	227.1	38.50	21.93	13.80	
BADGE-HCl	13836-48-1	**$[M+NH4]^+$**	**394.0**	**227.0**	42.89	19.78	14.17	0.48
		$[M+NH4]^+$	394.0	135.0	42.89	45.21	6.71	
BADGE-2HCl	4809-35-2	**$[M+NH4]^+$**	**431.3**	**229.0**	51.65	22.45	15.11	2.90
		$[M+NH4]^+$	431.1	227.0	54.59	23.48	13.81	
BFDGE	2095-03-6	**$[M+NH4]^+$**	**328.8**	**163.0**	41.97	19.35	8.93	0.24
		$[M+NH4]^+$	328.8	133.0	42.96	24.33	6.35	
SMXL-D4	1020719-86-1	**$[M+H]^+$**	**258.0**	**96.0**	56.36	45.25	17.08	NA
		$[M+H]^+$	258.0	112.0	72.14	35.41	5.62	

transitions in bold are quantitation ions NA = Not applicable

DP = Declustering potential CE = Collision energy CXP = Collision cell exit potential



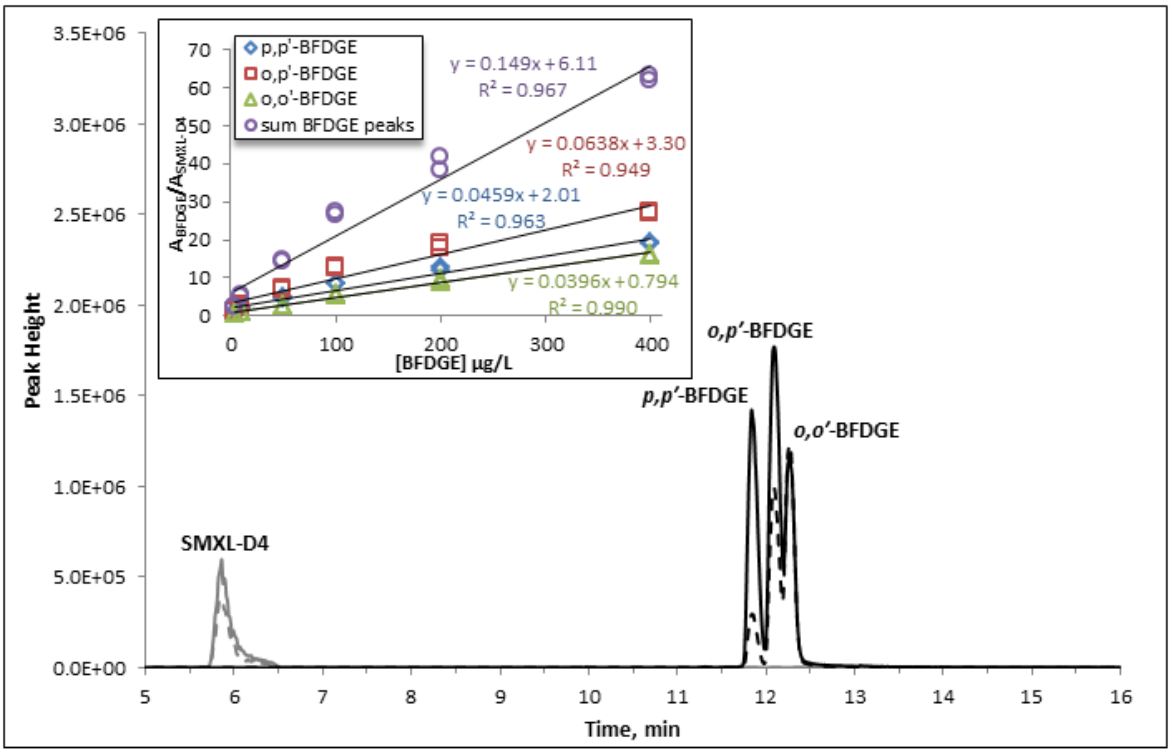


Figure 2.4 LC/MS/MS chromatogram of BDGE mix standard (296 µg/L BADGE, 294 µg/L BADGE-H_2O, 310 µg/L BADGE-2H_2O, 893 µg/L BADGE-H_2O-HCl, 204 µg/L BADGE-HCl, 805 µg/L BADGE-2HCl) along with a calibration curve (top) Chromatogram of an 800 µg/L BFDGE standard and calibration curve (bottom).

2.2.2.5 LC/MS/MS Analysis of Phthalic Acids (PAs)

The same LC/MS/MS system and chromatographic column used for the analysis of bisphenols was also used for phthalic acid analysis. A 50 µL aliquot of sample was injected at a flow rate of 0.4 mL/min. The gradient mobile phase was 0.1% formic acid and acetonitrile. The following percentages of acetonitrile were applied as the gradient: held at 15% for 3 min, then from 15% to 36% over 7.8 min, from 36% to 49% over 10.2 min, then 49% to 100% over 2 min, held at 100% for 2 min, and then returned to 15% over 5 min.

The quantitation ion for the PAs had a MRM transition of 165.00 → 120.91 and collision cell exit potential (CXP, volts) of -8.63, collision energy (CE, volts) of -17.45, and declustering potential (DP, volts) -52.58. The PAs confirmation ion had a MRM transition of 165.00 → 77.11 and CXP (volts) of -4.51, CE (volts) of -26.68, and DP (volts) -52.58. The internal standard (PA-D4) had a quantitation ion MRM transition of 169.16 → 81.10 and CXP (volts) of -3.55, CE (volts) of -22.59, and DP (volts) -25.89. The internal standard had a confirmation ion MRM transition of 169.16 → 81.10 and CXP (volts) of -7.07, CE (volts) of -15.26, and DP (volts) -28.91. The phthalic acids are isomers so it was not possible for separate MRM transition ions. Therefore, a specific acid was identified by its retention time, which was confirmed with a standard prior to every run, that is: PA was ~10.6 min, ~IPA 9.14 min, and TPA ~8.62 min (Figure 2.5). In reagent water, the MDLs were 1.4 µg/L, 0.53 µg/L, and 0.70 µg/L for PA, IPA, and TPA respectively. In dechlorinated tap water, 10% (by volume) acetonitrile was added to all samples and standards, and the MDLs were 4.0, 2.1, and 3.1 µg/L for PA, IPA, and TPA respectively.

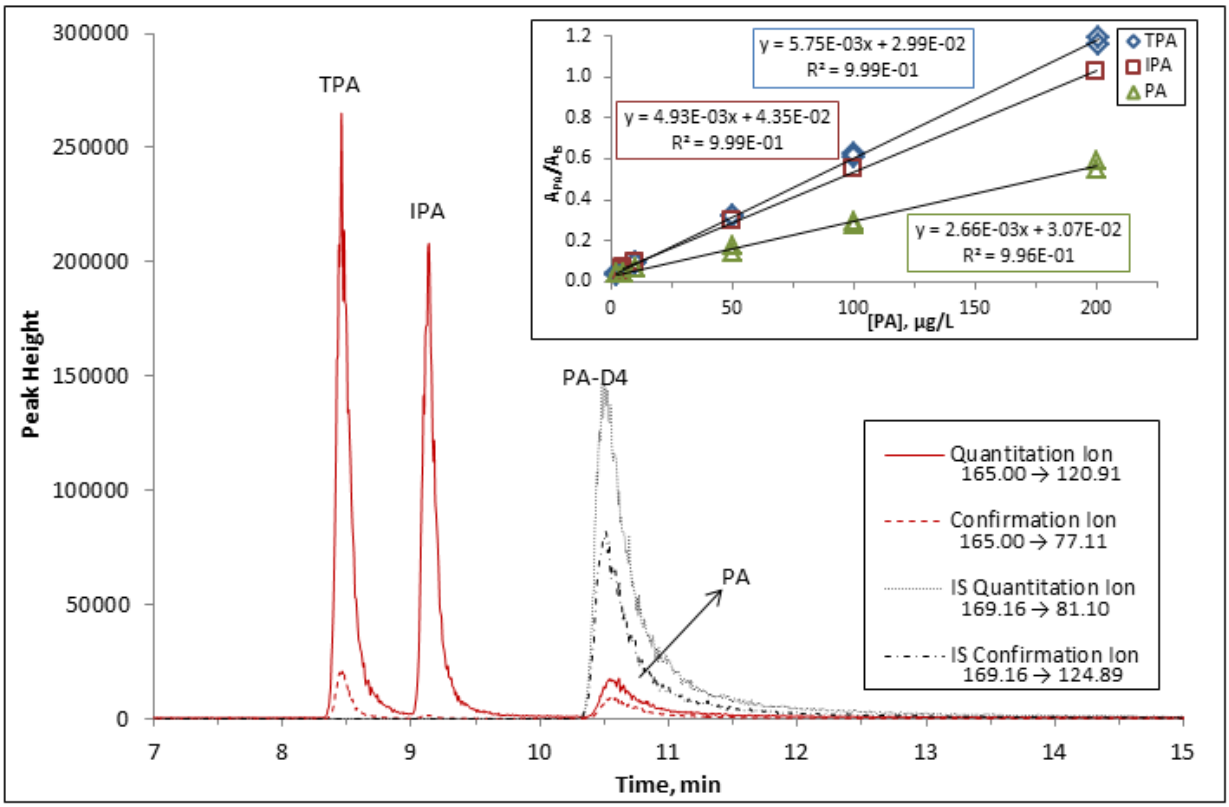


Figure 2.5 LC/MS/MS chromatogram and calibration curve for a 500 µg/L mixed phthalic acids standard.

2.2.2.6 GC/MS Analysis of Phthalate Esters

The same GC/MS system described in 2.2.2.4 was used for the analysis of phthalate esters. The column was a Varian FactorFour capillary column VF-5MS 0.32 mm ID, 30 m length, and 0.5 µm film thickness. Helium was used as the carrier gas and the transfer line temperature was 270°C. The sample solvent was hexanes/chloroform (50/50 by volume) with a 4.5 min solvent delay; a 1.0 µL splitless injection was made at an injection temperature of 270°C, and the carrier gas flow rate was 1.0 mL/min. The oven temperature started at 120°C and was ramped at 20°C/min to 200°C, then ramped at 30°C/min to 220°C, then ramped at 10°C/min to 250°C, held at 250°C for 5 min, then ramped at 10°C/min to 300°C, and held for 4 min. The MS was operated in SIM mode and transitions and elution times are reported in Table 2.3.

Prior to GC/MS analysis standards and samples were extracted by liquid liquid extraction (LLE). To a 20 mL sample aliquot, 500 g of sodium chloride and the surrogate internal standard (DNHP-D4) were added. The sample was extracted with 1 mL of chloroform, followed by a 1 mL extraction with hexane, and the organic layer was collected for analysis. The background level of the phthalates could not be reduced to below the noise (Figure 2.6 A); the background levels were reduced from those observed during initial method optimization but were never completely eliminated (Figure 2.6 B). The background levels varied between run days but were stable during the runs. A linear calibration curve based on the surrogate internal standard was used for quantitation and the S/N was used to determine the MDLs for each run day, which ranged from ≤ 1 to 10 µg/L (with a S/N of greater than 2 considered a relevant signal). The MDL was based on the S/N due to the low level variable phthalate background. A chromatogram with all the phthalate esters is provided in Figure 2.7.

Table 2.3 MS parameters for the GC/MS analysis of phthalate esters.

Compound	CAS Number	Retention Time, min	MS Ions Monitored Time, min	MS Ions Monitored Ions, Da
DMP	131-11-3	6.604	4.5 to 7.7	163.1 & 194.1
DMTP	120-61-6	7.136	4.5 to 7.7	163.1 & 194.1
DMIP	1459-93-4	7.243	4.5 to 7.7	163.1 & 194.1
DEP	84-66-2	8.063	7.7 to 10.0	149.1 & 177.1
DETP	636-09-9	8.892	7.7 to 10.0	149.1 & 177.1
DNBP	84-74-2	13.401	12.6 to 18.0	149.1 & 223.1
BBP	85-68-7	20.776	20.6 to 21.0	149.1 & 206.1
DEHA	103-23-1	21.126	21.0 to 22.5	129.1 & 147.1
DEHP	117-81-7	23.583	22.5 to 25.0	149.1 & 167.1
DNOP	117-84-0	26.158	25.0 to 26.7	149.1 & 279.1
DNHP-D4	1015854-55-3	20.276	18.0 to 20.6	153.1 & 255.1
PANE-D10	1517-22-2	11.657	10.0 to 12.6	160.0 & 188.2

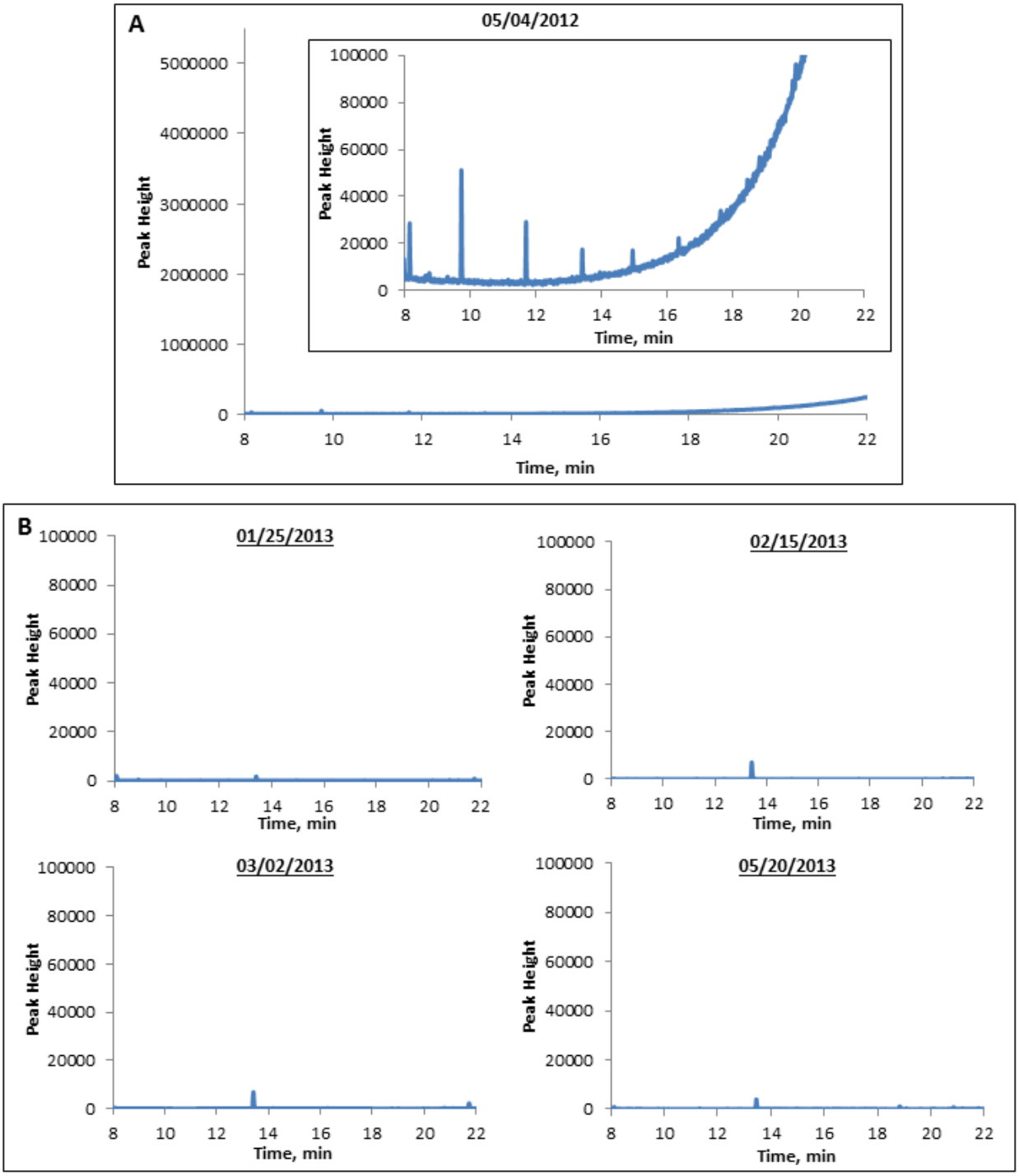


Figure 2.6 GC/MS chromatograms of a control blank used during analysis of phthalate esters. (A) Control blank used during the optimization of phthalate esters; inlay is a zoom of the sample showing low level phthalates in the background. (B) Control samples from different dates illustrating the variable low level phthalate background.

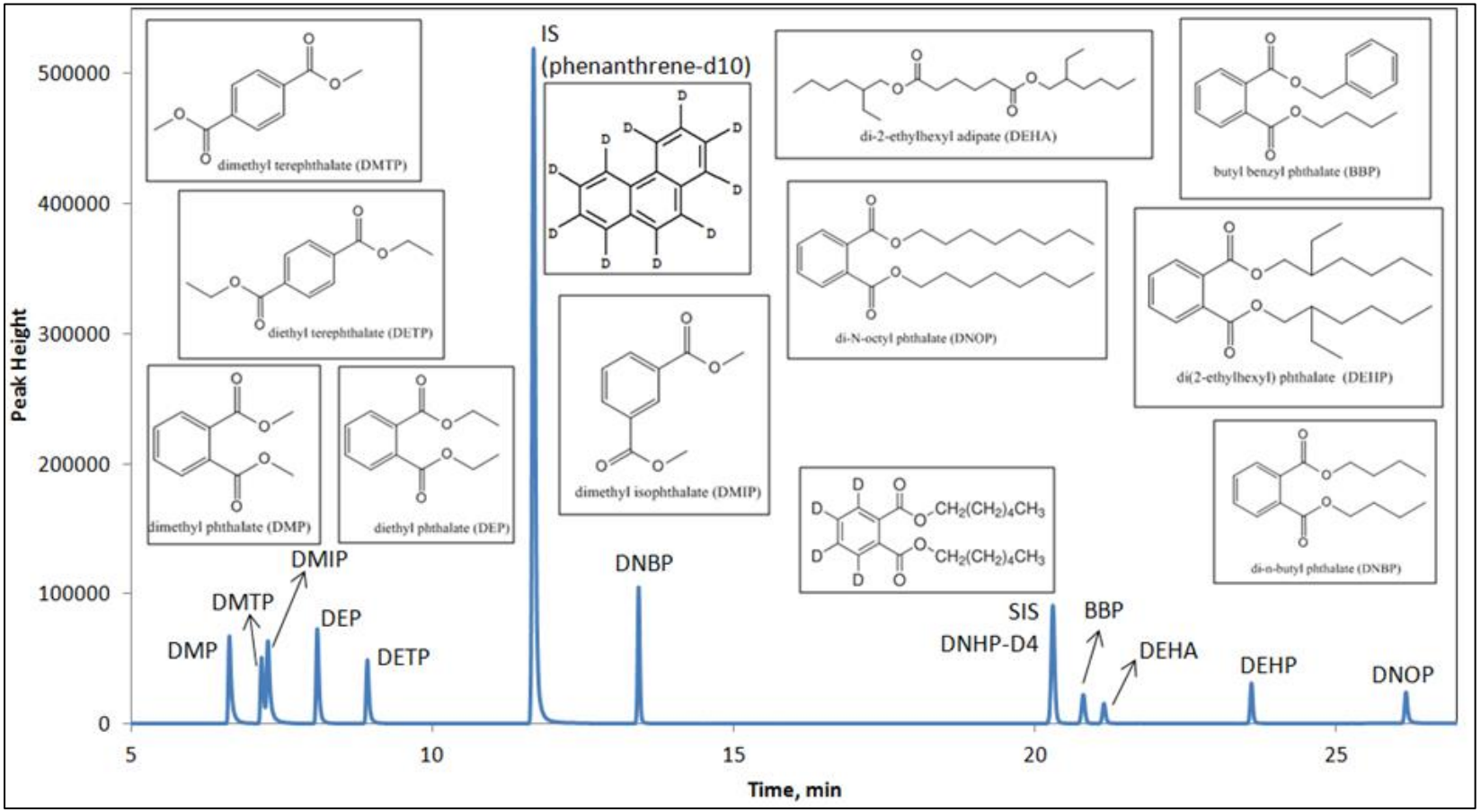


Figure 2.7 GC/MS with LLE extraction of an 800 µg/L mix phthalate ester standard.

2.2.2.7 Chlorine Analysis

Chlorine analysis was performed with methods developed for the Hach DR 5000 UV-Vis Spectrophotometer (Loveland, CO). Total chlorine solutions were prepared by dilution of a concentrated sodium hypochlorite stock solution and concentrations were determined using the EPA approved HACH Total Chlorine Method 8167 (based on the EPA DPD Method)[51], which determines residual chlorine concentration in units of mg/L as Cl_2. The sum of HOCl and OCl^- is referred to in practice as free chlorine (chlorine that is not combined with ammonia) and residual chlorine is the chlorine that remains in solutions.[52] During experiments initial free chlorine concentrations were within 0.2 to 4 mg/L, within the range of concentrations applicable to drinking water distribution systems. The EPA established chlorine maximum residual disinfectant level (MRDL) and maximum residual disinfectant level goals (MRDLG) is 4 mg/L as Cl_2.[53]

Monochloramine (MCA) solutions were prepared by spiking sodium hypochlorite into an ammonium chloride solution at pH 8.9, with the concentration chosen such that there was an ammonium excess of 0.1 mg/L as N (to ensure complete conversion of the hypochlorous acid to MCA). The MCA concentrations in mg/L as Cl_2 were determined using the Hach Chloramine (Mono) Indophenol Method 10200. The Hach Nitrogen, Free, Ammonia Indophenol Method 10200 was used to verify the ammonia excess.[54] MCA and other chloramine species formed when chlorine reacts with ammonia are collectively referred to in practice as combined chlorine.[52] During experiments initial combined chlorine concentrations were kept around 4 mg/L because the EPA's MRDL and MRDLG for combined chlorine is 4 mg/L as Cl_2.[53]

Chlorine quenching agents (i.e., sulfite, bisulfite, thiosulfate and ascorbic acid) were investigated, and sulfite or bisulfite was used to quench residual chlorine. The quenching agent was added such that excess was kept to a minimum.

2.2.3 Fill-and-Dump Experiments

2.2.3.1 End Fitting Leaching and Adsorption

End fitting materials in contact with the extraction water in the fill-and-dump experiments described below were investigated to evaluate possible artifacts, i.e., leaching or adsorption of the key leachates. Materials tested included silicone stoppers (LabPure® PX 18D and 21D, Saint-Gobain Performance Plastics, Portage, Wis.), linear high-density polyethylene (HDPE) stoppers (Type 16, Kimble Chase, Vineland, NJ), HDPE pipe nipples (5/8 in. ID x 3/4 in. OD; cut in 3-7/8 in. and 3-5/8 in. lengths from a 100 ft. roll; Grainger Part No. 2LZT9), unthreaded stainless steel (SS) pipe nipples (0.50 in. ID, about 5/8 in. actual ID, 3.0 in. long; Grainger Part No. 4NTN6; meeting ASTM A269/A213 and ASME SA213 standards), and threaded SS pipe nipples (0.50 in. ID, 5/8 in. actual ID, 2.50 in. long; Grainger Part No. 1XAB2; meeting ASTM Standard A733).

Two stoppered pipe nipple assemblages were constructed to test multiple end-fitting components simultaneously. The first assemblage consisted of two SS pipe nipples connected by a polypropylene compression fitting, and stoppered with silicone stoppers. The second assemblage was similar, but with HDPE pipe nipples instead of SS pipe nipples (Figure 2.8). In these tests for possible artifacts, the surface area-to-volume ratios of the end-fittings were significantly higher than those anticipated in the fill-and-dump experiments (Tables 2.4 and 2.5). For example, the surface-to-volume ratios for the leaching and adsorption tests on the

Figure 2.8 Various end-fittings used on pipe sections for fill-and-dump experiments. At top left are pipe sections with stainless steel pipe nipples at the ends, at top right are the end-fitting assemblages used to test multiple components, and at the bottom are silicone and HDPE stoppers in LSL (back) and CSL (front) sections. Top left and bottom images are used by permission of Zachary Breault.

Table 2.4 Surface area-to-volume ratios for end-fitting leaching and adsorption experiments with bisphenols (BPs) and bisphenol diglycidyl ethers (BDGEs).

Analytes	End-fitting Component	Experiment	Surface Area/Volume cm^2/mL	Test Solutions	Sampling Times
BPs	silicone stopper	adsorption	0.957	~20 µg/L BP mix standard, 5 mM phosphate buffered at pH 7	0, 24 hours
BPs	silicone stopper	leaching	0.956	5 mM phosphate buffered reagent water at pH 7	0, 24 hours
BPs	silicone stopper	leaching	0.956	HOCl 2 mg/L as Cl_2 phosphate buffered at pH 7	0, 24 hours
BPs	assemblage[§]	adsorption	2.04**	~20 µg/L BP mix standard, 5 mM phosphate buffered at pH 7	0, 24 hours
BPs	assemblage[§]	leaching	2.04**	5 mM phosphate buffered reagent water at pH 7	0, 24 hours
BDGEs	silicone stopper	adsorption	0.175	~175 µg/L BADGE standard in pH 8 extraction water*	0, 6, 24, 96 hours
BDGEs	silicone stopper	adsorption	0.0158	~600 µg/L BADGE standard in pH 8 extraction water*	0, 6, 24, 96 hours
BDGEs	SS pipe	adsorption	1.305	~500 µg/L BADGE standard in pH 8 extraction water*	0, 0.25, 1, 4, 9 days
BDGEs	SS thread	adsorption	0.534	~500 µg/L BADGE standard in pH 8 extraction water*	0, 0.25, 1, 4, 9 days
BDGEs	silicone stopper	leaching	0.175	pH 8 extraction water*	0, 3.5, 9.5 days
BDGEs	SS pipe	leaching	0.287	pH 8 extraction water*	0, 3.5, 9.5 days
BDGEs	SS thread	leaching	0.534	pH 8 extraction water*	0, 3.5, 9.5 days

[§]testing of both pipe assemblages

*pH 8 extraction water = 0.56 mM $NaHCO_3$, 1mM $CaCl_2$, 0.44 mM NaCl in reagent water (which has a pH value of ~8 without adjustment and is the same as the chlorinated pH 8 reagent water used in FD2 except that no chlorine was added)

**based on the surface area of the nipples and stoppers

Table 2.5 Surface area-to-volume ratios for end-fitting leaching and adsorption experiments with phthalate esters (PAEs) and phthalic acids (PAs).

Analytes	End-fitting Component	Experiment	Surface Area/Volume cm^2/mL	Test Solutions	Sampling Times
PAEs	silicone stopper	adsorption	0.278	~200 µg/L PAE standard mix in pH 8 extraction water*	0, 0.83, 6 days
PAEs	HDPE stopper	adsorption	0.128	~200 µg/L PAE standard mix in pH 8 extraction water*	0, 0.75, 7 days
PAEs	SS pipe	adsorption	1.742	~200 µg/L PAE standard mix in pH 8 extraction water*	0, 0.83, 6 days
PAEs	SS thread	adsorption	0.397	~200 µg/L PAE standard mix in pH 8 extraction water*	0, 0.83, 6 days
PAEs	silicone stopper	leaching	0.362	H_2O:MeOH (90:10)	0, 19, 72 hours
PAEs	silicone stopper	leaching	0.362	hexane:chloroform (50:50)	0, 19, 72 hours
PAEs	HDPE stopper	leaching	0.136	H_2O:MeOH (90:10)	0, 0.92, 7 days
PAEs	HDPE stopper	leaching	0.136	hexane:chloroform (50:50)	0, 0.92, 7 days
PAEs	SS pipe	leaching	1.746	H_2O:MeOH (90:10)	0, 19, 72 hours
PAEs	SS pipe	leaching	1.746	hexane:chloroform (50:50)	0, 19, 72 hours
PAEs	SS thread	leaching	0.391	H_2O:MeOH (90:10)	0, 19, 72 hours
PAEs	SS thread	leaching	0.391	hexane:chloroform (50:50)	0, 19, 72 hours
PAs	silicone stopper	adsorption	0.278	~100 µg/L PA standard mix in pH 8 extraction water**	0, 10, 96 hours
PAs	HDPE stopper	adsorption	0.128	~120 µg/L PA standard mix in pH 8 extraction water*	0, 0.83, 7 days
PAs	SS pipe	adsorption	1.742	~100 µg/L PA standard mix in pH 8 extraction water*	0, 10, 96 hours
PAs	SS thread	adsorption	0.397	~100 µg/L PA standard mix in pH 8 extraction water*	0, 10, 96 hours
PAs	silicone stopper	leaching	0.373	H_2O:MeOH (90:10)	0, 19, 72 hours
PAs	silicone stopper	leaching	0.373	acetonitrile	0, 19, 72 hours
PAs	HDPE stopper	leaching	0.151	H_2O:MeOH (90:10)	0, 0.92, 7 days
PAs	HDPE stopper	leaching	0.151	acetonitrile	0, 0.92, 7 days
PAs	SS pipe	leaching	1.740	H_2O:MeOH (90:10)	0, 19, 72 hours
PAs	SS pipe	leaching	1.740	acetonitrile	0, 19, 72 hours
PAs	SS thread	leaching	0.400	H_2O:MeOH (90:10)	0, 19, 72 hours
PAs	SS thread	leaching	0.400	H_2O:MeOH (90:10)	0, 19, 72 hours

*pH 8 extraction water = 0.56 mM $NaHCO_3$, 1mM $CaCl_2$, 0.44 mM NaCl in reagent water (which has a pH value of ~8 without adjustment and is the same as the chlorinated pH 8 reagent water used in FD2 except that no chlorine was added)

silicone and HDPE stoppers ranged from 0.128 to 0.957 cm^2/mL, whereas the approximate surface area-to-volume ratios for the stoppers in the fill-and-dump experiments was 0.0127 cm^2/mL (assuming 3.30 cm^2 exposed surface area and 260 mL of extracted water in a 4 ft. long lined or coated pipe section).

In the fill-and-dump experiments, contact between the extraction waters and the pipe nipples was negligible. Pipe nipples were attached to both ends of each pipe section so the lining or coating could be extended past the cut ends of each lead or copper pipe section, thereby preventing the extraction water from coming into contact with the lead or copper.[55] Exposure of the extraction water to the pipe nipples was negligible for lined or coated pipe sections because extraction waters came into contact only with the end of a pipe nipple, and only very briefly, as they were poured out into a glass beaker.

For leaching studies, the end-fitting components were placed individually into beakers and submerged in various solutions and solvents (test solutions), and sampled periodically for bisphenols (i.e., BPA, BPB, BPD, BPE, BPF), BDGEs (i.e., BADGE, BADGE-H_2O, BADGE-$2H_2O$), phthalate esters (i.e., BBP, DNBP, DNOP, DMTP, DMP, DMIP, DEP, DETP, DEHA, DEHP), and phthalic acids (i.e., PA, IPA, TPA). The pipe assemblages were filled with the test solutions and sampled periodically for the bisphenols. Controls during these studies were the test solutions and solvents with no contact with end-fittings. During adsorption studies the end-fittings were individually submerged in the analyte test solutions and sampled over time; controls were the analytes test solutions (no contact with end-fittings). These test solutions and the sampling intervals are specified in Tables 2.4 and 2.5.

2.2.3.2 Epoxy Coating Fill-and-Dump Experiment 1 (FD1)

The purpose of the first set of fill-and-dump experiments (FD1) was to examine organic compounds leached from freshly applied epoxy coatings. For the initial fill-and-dump investigation (FD1), a potable water grade epoxy coating was applied by the manufacturer to the inside of each lead or copper service line, except for the controls, which were unlined lead and copper pipe sections. The epoxy was cured for 48 hours and the pipe sections were then flushed for 15 min with cold tap water to remove any particles or readily dissolved materials.[56]

The extraction waters used to fill the pipe sections were similar to those specified by the National Sanitation Foundation (NSF)[35]; differences from the specifications of NSF meant equivalent results would not necessarily be obtained. Three extraction waters were used: dechlorinated pH 8 tap water (DT), chlorinated pH 8 extraction water (CL), and pH 6.5 extraction water (LP, with the lower pH intended to more aggressively solubilize metals, especially lead and copper). The dechlorinated pH 8 tap water was prepared by dechlorinating with sodium bisulfite (with chlorine removal confirmed using HACH Total Chlorine Method 8167[51]) and then adjusting the pH of tap water to 8.0 ± 0.1 using 1.0 or 0.1 N HCl and 0.1 N NaOH. Chlorinated pH 8 extraction water was 1 mM sodium bicarbonate, with 1 mM $CaCl_2$ added as a source of water hardness, sodium hypochlorite solution added to produce a free chlorine residual of 2 mg/L as Cl_2, and the pH adjusted to 8.0 ± 0.1 using HCl or NaOH. The pH 6.5 extraction water was 1 mM sodium carbonate, with 1 mM $CaCl_2$ added as a source of water hardness and the pH adjusted to 6.5 ± 0.1 with HCl or NaOH. The extraction waters were held in the pipe sections (with silicone stoppers) at room temperature (controlled at 20–25 °C) for

0.25, 1, 4, 7, and 10 days and then analyzed for bisphenols (BPA, BPB, BPD, BPE, and BPF) and BADGE.[56,57] The order of pipe section reuse during FD1 is indicated in Table 2.6.

2.2.3.3 Epoxy Coating Fill-and-Dump Experiment 2 (FD2)

The purpose of the second fill-and-dump experiment (FD2) was to examine leaching after the pipe sections from FD1 were stored wet or dry. FD2 was performed with selected epoxy-coated pipes used in FD1, the uncoated (control) pipe sections from FD1, and two epoxy-coated pipes that had been stored dry (for additional curing time) and were not filled during FD1. All of the pipes had been stored at room temperature for seven months. Some were stored wet (filled with reagent water) and some dry. After being removed from storage (and emptied if needed), the pipe sections were rinsed with 100 mL of reagent water and then filled with chlorinated pH 8 extraction water. The extraction water was prepared as before, but with 0.56 mM sodium bicarbonate and 0.44 mM NaCl) instead of 1 mM sodium bicarbonate, so that the initial pH would be about 8.0 and would require little or no adjustment. The extraction water was held in the pipe sections at room temperature (20-25 °C) for 6 to 24 h. After samples were collected for analysis of bisphenols and BADGE, the pipe sections were refilled with chlorinated pH 8 extraction water and held for 7 more days before a second set of samples was collected.

All pipe sections were then flushed for 15 min with cold tap water, rinsed with 100 mL of reagent water, and then refilled with chlorinated pH 8 extraction water. Six hours later, samples were collected for analysis of bisphenols and BADGE. The pipe sections were then refilled, held for 1 d and sampled again, then refilled and then held for 7 d. In every case, the pipe sections were stored at room temperature. The order of pipe section reuse during FD2 is

indicated in Table 2.6. The detailed SOP for the FD1 and FD2 experiments are provided in Appendix sections A.1.6, A.1.7, A.1.8, and A.1.9.

2.2.3.3 PET Liner Fill-and-Dump Experiment (FD3)

A fill-and-dump experiment (FD3) was performed to study leaching of organic compounds from PET liners. A potable-water-grade PET liner was installed by the manufacturer inside each of a series of LSL and CSL pipe sections (described earlier, and not previously used for experimental purposes), except for the controls, which were unlined lead and copper pipe sections. Prior to filling with extraction water the pipe sections were flushed for 15 min with cold tap water to remove any particles or readily dissolved materials.

The extraction waters were similar to those described for FD1 and FD2. The dechlorinated tap water was prepared by dechlorinating with sodium bisulfite (with chlorine removal confirmed using HACH Total Chlorine Method 8167[51]) and then adjusting the pH to 8.0 ± 0.1 using 1.0 or 0.1 N HCl and 0.1 N NaOH. Chlorinated pH 8 extraction water was 0.56 mM sodium bicarbonate and 0.44 mM NaCl, with 1 mM $CaCl_2$ added as a source of water hardness and sodium hypochlorite solution added to produce a free chlorine residual of 2 mg/L as Cl_2. The was pH adjusted, if necessary, to 8.0 ± 0.1 using HCl or NaOH. The pH 6.5 extraction water was 0.018 mM sodium carbonate and 0.98 mM NaCl, with 1 mM $CaCl_2$ added as a source of water hardness and the pH adjusted to 6.5 ± 0.1 with HCl or NaOH. Each pipe section was first rinsed with 100 mL of designated extraction water, and then filled with the same extraction water. The extraction waters were held in the pipe sections (with HDPE stoppers) at room temperature (controlled at 20–25 °C) for 0.25, 1, and 4 days and then analyzed for phthalic acids and phthalate esters. Table 2.7 shows the pipe history and the SOP with additional

Table 2.6 Filling order history and holding time of the controls and epoxy coated pipe sections during fill-and-dump experiments FD1 and FD2.

Pipe Section	FD1 Extraction Water and Holding Time (Sequential Filling Order →)			Storage Condition*	FD2 Extraction Water & Holding Time (Sequential Filling Order →)					
Pb01	DT, 6 h	LP, 6 h	LP, 168 h	dry			Pipe sections flushed 15 min with tap water, then rinsed with 100 mL extraction water			
Pb02	DT, 6 h	LP, 6 h	LP, 168 h	wet	CL, 24 h	CL, 168 h		CL, 6 h	CL, 24 h	CL, 168 h
Pb03	CL, 6 h	LP, 6 h	LP, 168 h	dry						
Pb04 (Control)	DT, 6 h	LP, 6 h	LP, 168 h	dry	CL, 6 h	CL, 168 h				
Pb05	DT, 24 h	DT, 240 h		dry	CL, 24 h	CL, 168 h		CL, 6 h	CL, 24 h	CL, 168 h
Pb06	CL, 24 h	CL, 240 h		dry						
Pb07	DT, 96 h			dry						
Pb08	CL, 96 h			dry	CL, 6 h			CL, 6 h	CL, 24 h	CL, 168 h
Pb09				dry	CL, 24 h	CL, 168 h		CL, 6 h	CL, 24 h	CL, 168 h
Cu01	DT, 6 h	LP, 6 h	LP, 168 h	dry						
Cu02	DT, 6 h	LP, 6 h	LP, 168 h	wet	CL, 24 h	CL, 168 h		CL, 6 h	CL, 24 h	CL, 168 h
Cu03	CL, 6 h	LP, 6 h	LP, 168 h	dry						
Cu05	DT, 24 h	DT, 240 h		dry	CL, 24 h	CL, 168 h		CL, 6 h	CL, 24 h	CL, 168 h
Cu06	CL, 24 h	CL, 240 h		dry						
Cu07	DT, 96 h			dry						
Cu08	CL, 96 h			dry	CL, 6 h			CL, 6 h	CL, 24 h	CL, 168 h
Cu09				dry	CL, 24 h	CL, 168 h		CL, 6 h	CL, 24 h	CL, 168 h
Cu10 (Control)	DT, 6 h	LP, 6 h	LP, 168 h	dry	CL, 6 h	CL, 168 h				

*Stored for 7 months at room temperature (20-25 °C)

Table 2.7 Filling order history and holding times of the controls and PET lined pipe sections during fill-and-dump experiment FD3.

Pipe Section	PET FD Extraction Water and Holding Time (Sequential Filling Order →)		
Pb11 (Control)	DT, 6 h	LP, 6 h	LP, 96 h
Pb12	DT, 6 h	LP, 6 h	LP, 96 h
Pb13	DT, 6 h	LP, 6 h	LP, 96 h
Pb14	CL, 6 h	LP, 6 h	LP, 96 h
Pb15	DT, 24 h		
Pb16	CL, 24h		
Pb17	DT, 96 h		
Pb18	CL, 96 h		
Cu11 (Control)	DT, 6 h	LP, 6 h	LP, 96 h
Cu12	DT, 6 h	LP, 6 h	LP, 96 h
Cu13	DT, 6 h	LP, 6 h	LP, 96 h
Cu14	CL, 6 h	LP, 6 h	LP, 96 h
Cu15	DT, 24 h		
Cu16	CL, 24h		
Cu17	DT, 96 h		
Cu18	CL, 96 h		

information is in Appendix section A.1.10.

2.3 Results and Discussion

2.3.1 Method Development Notes

2.3.1.1 Syringe Filter Leaching and Adsorption of Bisphenols

To prevent clogging of the LC column and LC system with debris from the unlined and uncoated control pipe sections, the bisphenols samples collected during FD1 and FD2 were syringe filtered prior to analysis. Four syringe filters materials were investigated to ensure they did not leach or adsorb bisphenols (Figure 2.9). The mixed cellulose ester (MCE) filter did not leach any bisphenols and adsorbed 23% of the BPD starting concentration. The polytetrafluoroethylene (PFTE) filter did not leach bisphenols and adsorbed 36% of the BPD starting concentration. The polycarbonate (PC) filter leached 3.46 (± 0.44) µg/L of BPA and adsorbed 10% of the BPD starting concentration. The nylon filter adsorbed 100% of the starting BPA, BPB, BPE, and BPF concentrations (while BPD was not tested). MCE was selected as the filter membrane because it did not leach bisphenols and had relatively low adsorption of BPD.

2.3.1.2 Chlorine Quenching Agents and Bisphenols

A quenching agent is required during chlorination experiments to obtain data at specific time points. Potential quenching agents for chlorine include ascorbic acid, sulfites (e.g., sodium sulfite and sodium bisulfite), and sodium thiosulfate. During experiments, a quenching agent needs to be added in slight excess to ensure that all chlorine is quenched. Changes in solution matrix (by addition of quenching agents) can alter the ionization efficiency of the MS electrospray. Therefore, experiments were conducted to determine which quenching agent would have minimal impact on the electrospray.

A bisphenol standard was prepared in reagent water and then in varied concentrations of ascorbic acid, sodium sulfite, sodium bisulfite, and sodium thiosulfate. The LC/MS/MS response factors are shown in Figures 2.10 and 2.11. BPA in 10 mg/L ascorbic acid had relatively the same response as BPA in reagent water, while the BPA in 25 mg/L ascorbic acid was slightly suppressed, BPA in 7 mg/L sodium sulfite was slightly enhanced, BPA in 25 mg/L sodium bisulfite and in 8 mg/L sodium thiosulfate were relatively the same as in reagent water, and BPA in 18 mg/L sodium thiosulfate was significantly enhanced. BPB followed the same trend except that the response factor in 7 mg/L sodium sulfite was relatively the same as in reagent water. The BPE and BPF trends were the same as for BPA with the expectation that both ascorbic acid concentrations yielded about the same response when compared to reagent water. Sodium bisulfite at a relatively high concentration did not significantly enhance or suppress the relative responses, so it was tentatively chosen as the quenching agent.

To evaluate a lower sodium bisulfite quenching concentration, bisphenols were prepared in a 6 mg/L sodium bisulfite solution Figure 2.12. The response factors of the bisphenols were similar and only slightly suppressed, with ~10% difference between reagent water and 6 mg/L sodium bisulfite. Sample concentrations were calculated using a calibration curve prepared in reagent water and only ~10% difference noted. Sodium bisulfite was selected as the quenching agent because it would not significantly suppress or enhance the BPA signal at high concentrations and only moderately at 6 mg/L. Bisulfite concentrations in quenched samples would be significantly lower, because most of it would be consumed by reacting with residual chlorine and only a slight excess would remain.

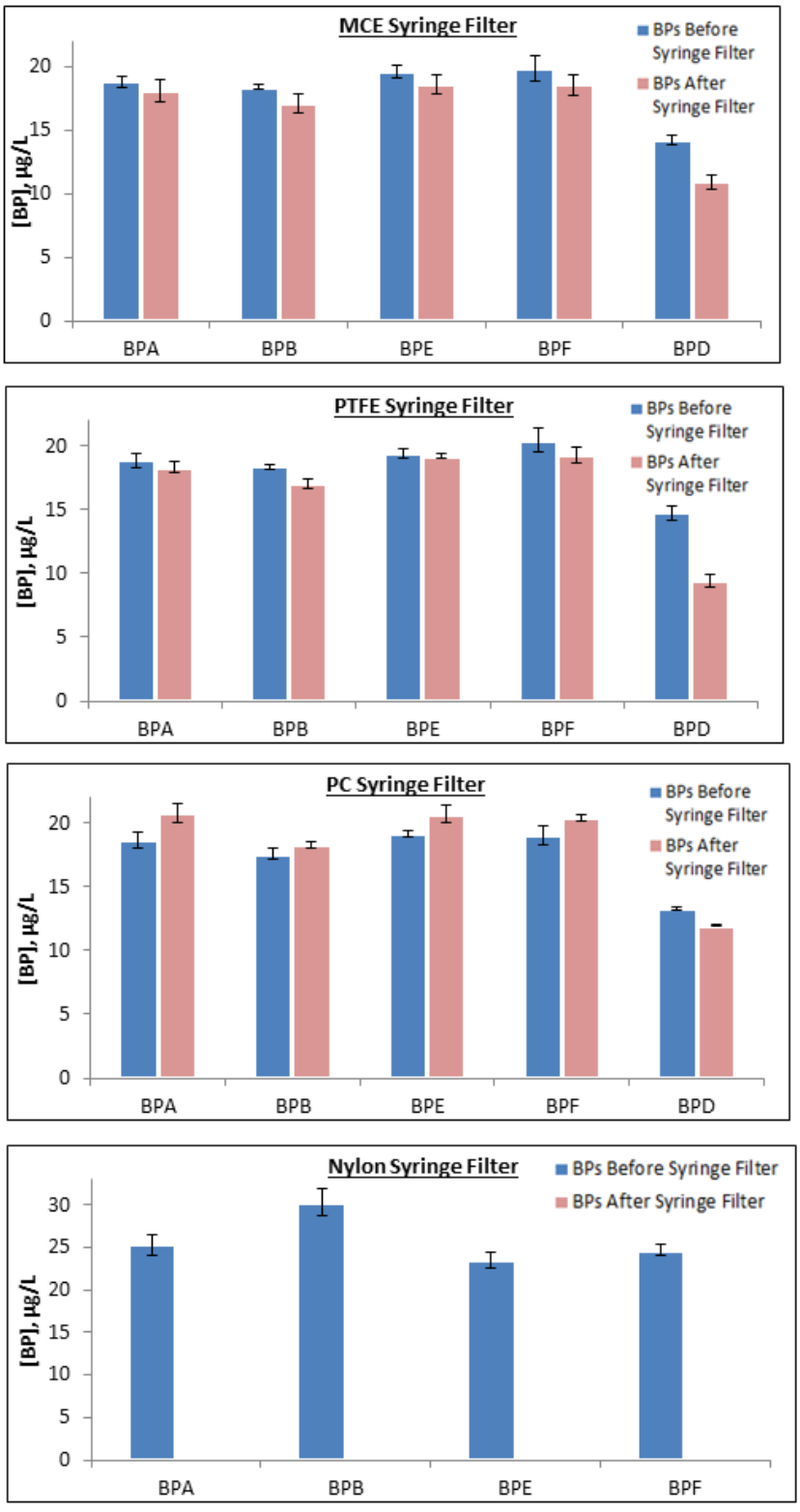


Figure 2.9 Bisphenol adsorption to syringe filters with error bars based on the standard deviation of n = 3 (three replicate filter samples).

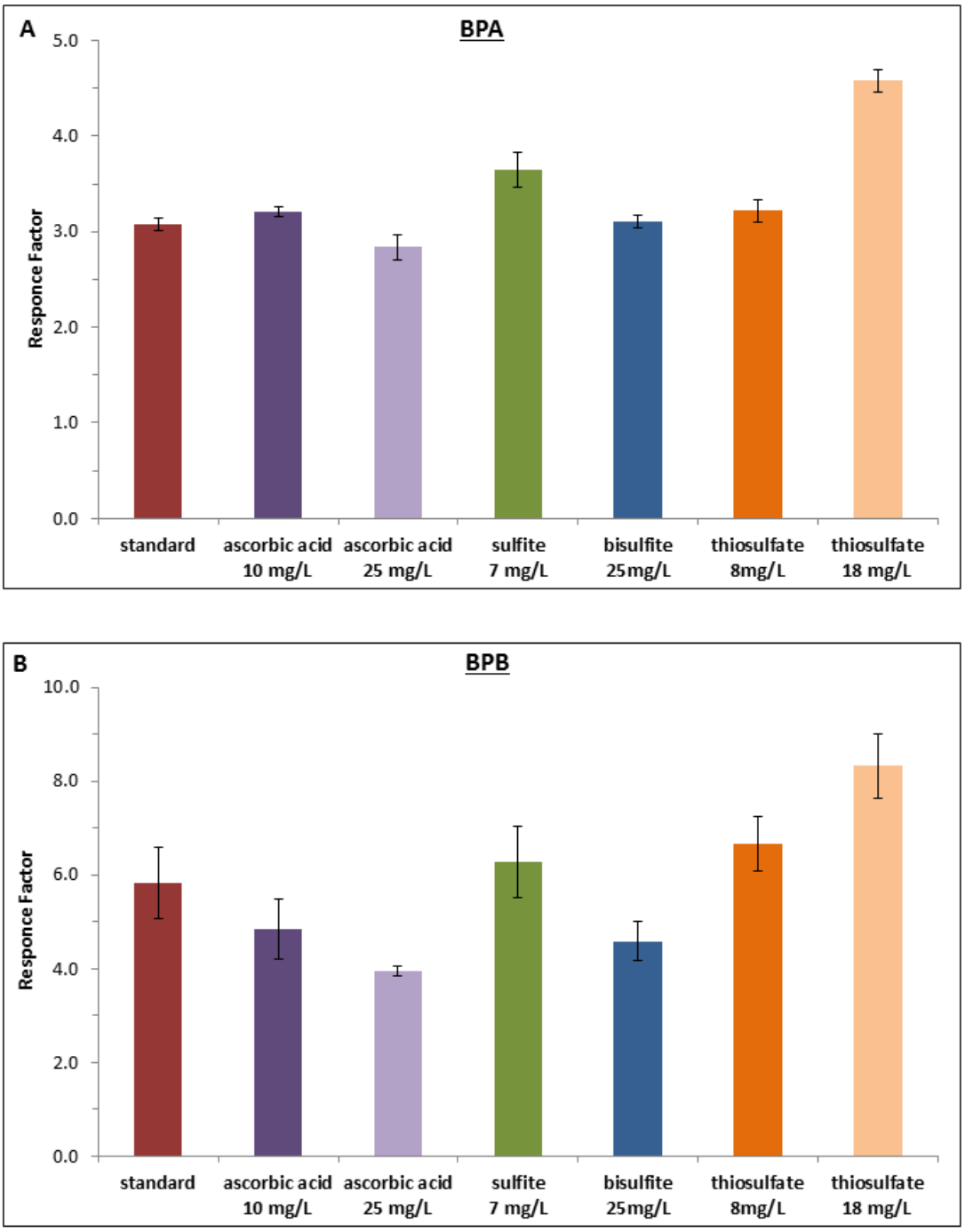


Figure 2.10 LC/MS/MS response factors comparing a bisphenol standard (20 µg/L) in reagent water (labeled as standard) to bisphenol standard (20 µg/L) in various concentrations of quenching agents for (A) BPA and (B) BPB. Error bars are the standard deviations of n = 5 replicate injections.

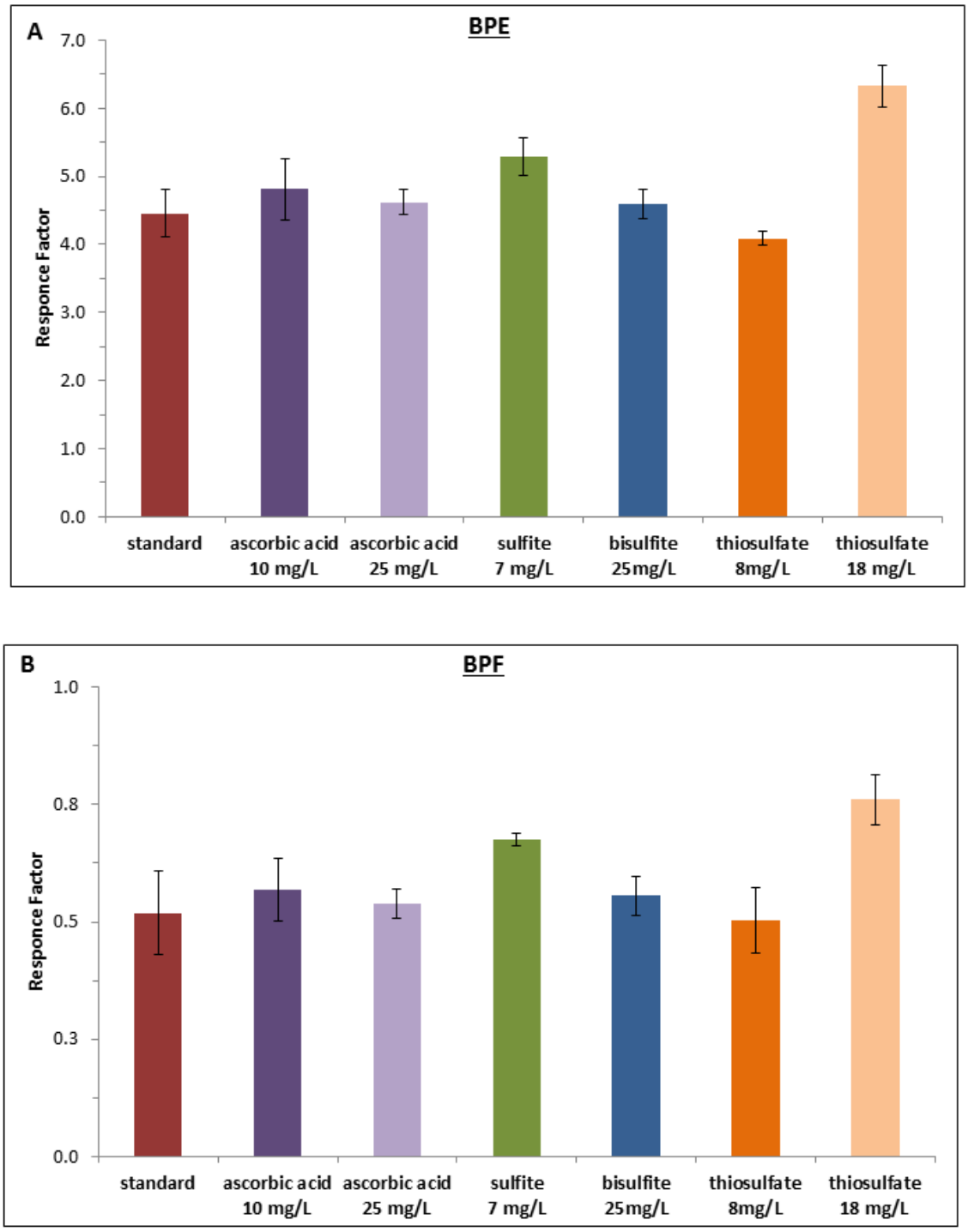


Figure 2.11 LC/MS/MS response factors comparing a bisphenol standard (20 µg/L) in reagent water (labeled as standard) to bisphenol standard (20 µg/L) in various concentrations of quenching agents for (A) BPE and (B) BPF. Error bars are the standard deviations of n = 5 replicate injections.

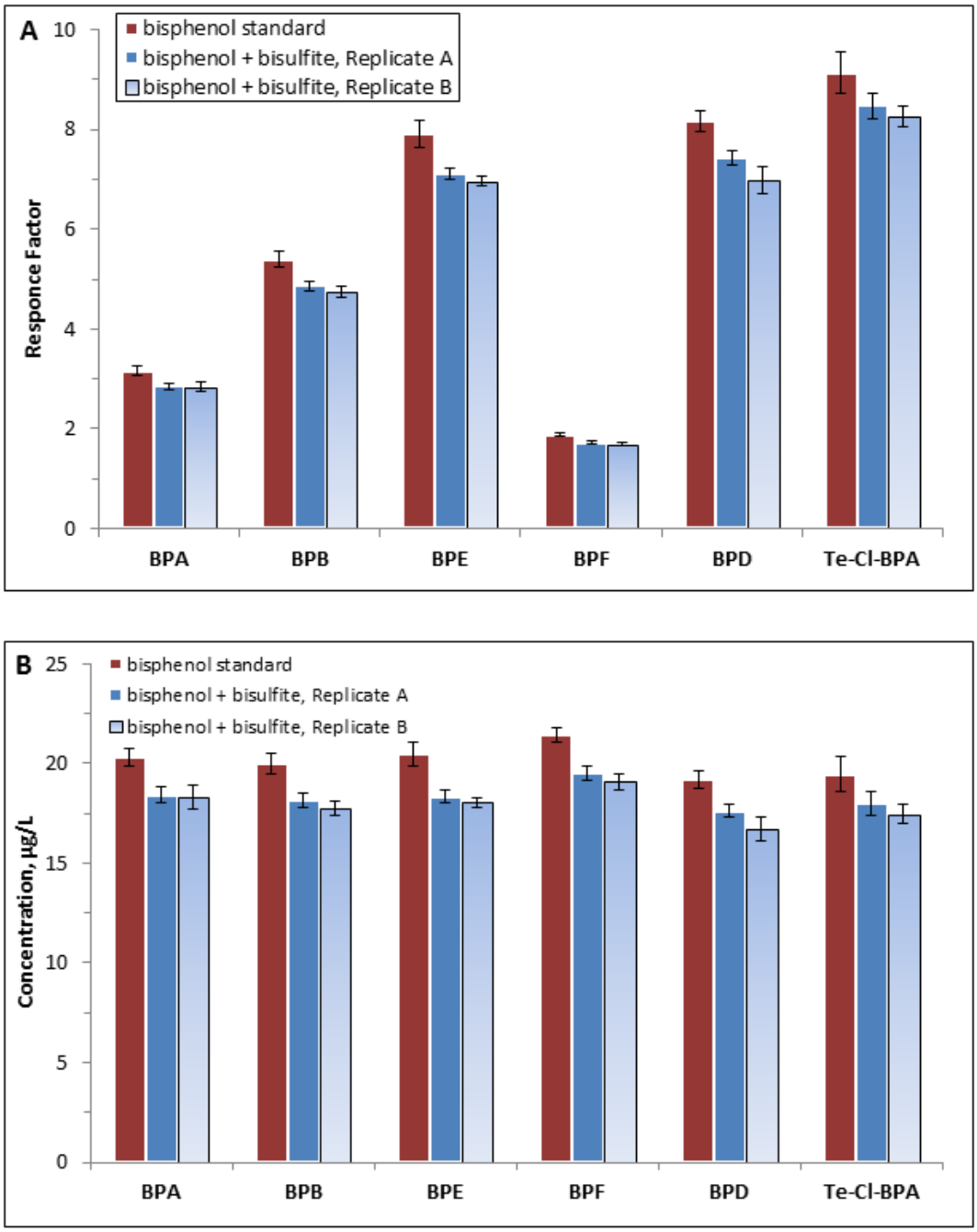


Figure 2.12 Comparison of a bisphenol mix standard (20 µg/L) prepared in reagent water to that of a 20 µg/L mix prepared in 6 mg/L sodium bisulfite. Error bars are the standard deviations of n = 5 replicate injections. (A) Comparison of bisphenol response factors. (B) Comparison of calculated bisphenol concentrations using a calibration curve prepared in reagent water.

2.3.1.3 Phthalic Acids Standard Stability

During LC/MS/MS optimization phthalic acids were noted to be unstable under certain conditions. The phthalic acids were stable in reagent water and for 20 hours (or 1250 min) in extraction water (i.e., reagent water with 0.56 mM $NaHCO_3$, 1 mM $CaCl_2$, and 0.44 mM NaCl at pH 8) (Figure 2.13 A and B). However, when a mixed PA standard solution was prepared in dechlorinated tap water, PA and the internal standard were stable (Figure 2.13, C) but IPA and TPA significantly degraded after 9 hours (Figure 2.13 D). Addition of 10% and 20% acetonitrile (by volume) was investigated as a means to increase stability. The results show that 10% addition stabilized IPA and slowed TPA decay (Figure 2.13 E), while the 20% addition stabilized both (Figure 2.13 F). To keep the acetonitrile addition low, 10% acetonitrile was added to all samples and standards, and the total run time was kept to 12 hours (or 720 minutes) or less, thereby limiting TPA decay to less than 20%.

2.3.2 Preliminary Chlorination Investigation

One specific aim of the dissertation research is to determine the chlorine reactivity of key leachates, thus aiding in the development of kinetic models predicting drinking water analyte stability. To determine potential by-products from the reaction of leachates with chlorinated water, standards of the key leachates were exposed to chlorine solutions as a preliminary experiment. This data helped to determine the sampling timescales for the kinetic studies with chlorine (Chapter 5) and provided information about possible reactions in the fill-and-dump studies (when chlorinated extraction water was used).

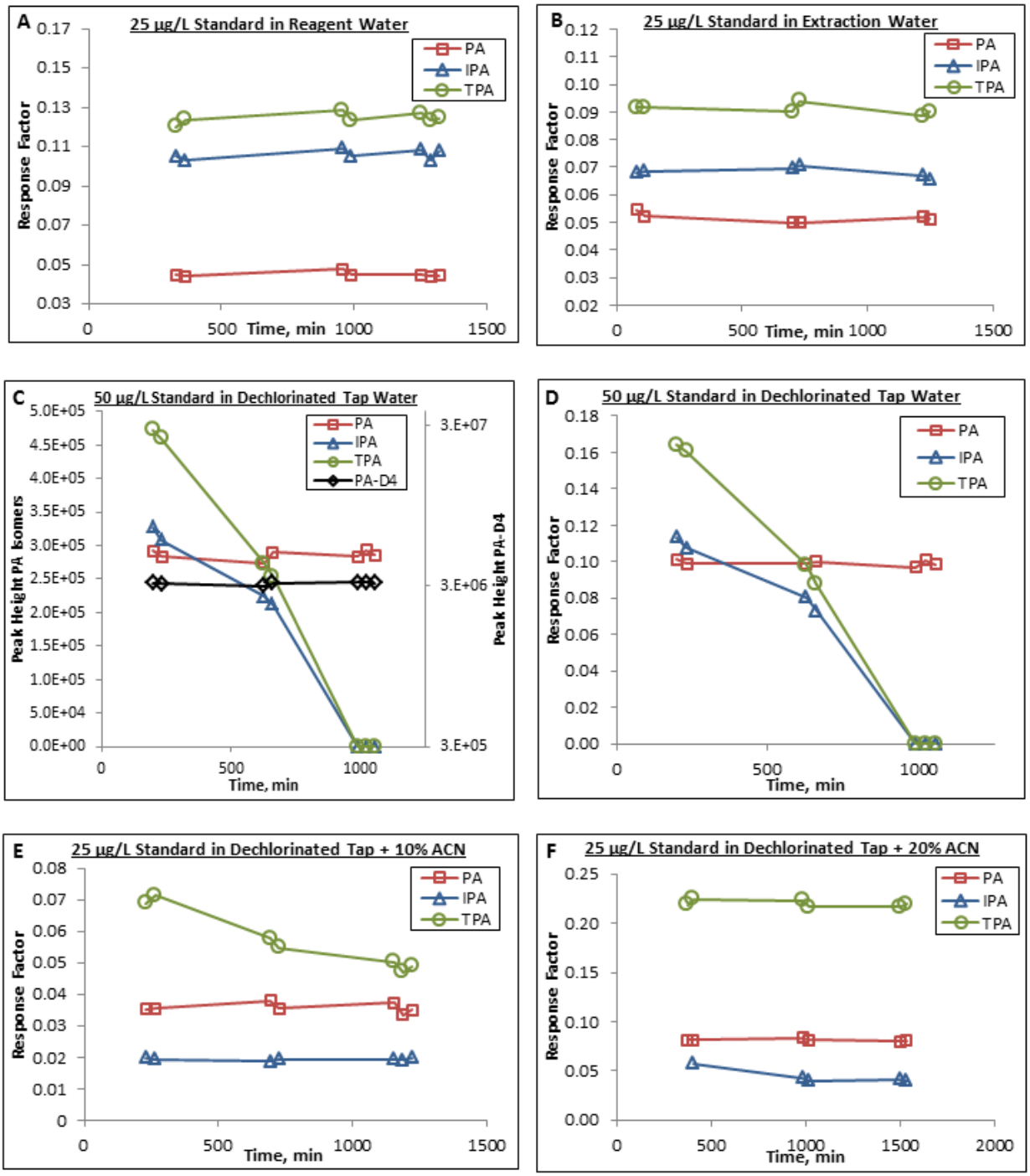


Figure 2.13 Stability of phthalic acid isomers. (A) Response factors of a 25 µg/L mixed PAs standard prepared in reagent water. (B) Response factors of a 25 µg/L mixed PAs standard prepared in in extraction water (reagent water with 0.56 mM $NaHCO_3$, 1 mM $CaCl_2$, and 0.44 mM NaCl at pH 8). (C) Peak heights of a 50 µg/L mixed PAs standard prepared in dechlorinated tap water. (D) Response factors of a 50 µg/L mixed PAs standard prepared in dechlorinated tap water. (E) Response factors of a 25 µg/L mixed PAs standard prepared in dechlorinated tap water with 10% acetonitrile. (F) Response factors of a 25 µg/L mixed PAs standard prepared in dechlorinated tap water with 20% acetonitrile.

2.3.2.1 Chlorination and Monochloramination of Bisphenols

To investigate bisphenol chlorine reactivity, a 20 µg/L bisphenol solution (of BPA, BPD, BPB, BPE, and BPF) was spiked with a sodium hypochlorite solutions to produce a free chlorine residual of 2 mg/L as Cl_2 (pH = 7). After 24 hours of contact time (at room temperature, 20-25 °C) the solution was analyzed and no bisphenols were detected, suggesting all the bisphenols had been chlorinated. The experiment was repeated at pH 7.6 and 9.6 and a 20 µg/L mixed bisphenol standard in reagent water was used as a control. Analysis was performed at shorter contact times, but the bisphenols decayed rapidly, dropping to below detection limit after only one hour of contact time (Figure 2.14). To slow the reaction, the concentration of the free chlorine was reduced to 0.2 mg/L as Cl_2 and a slow decay of the bisphenols was observed over 10 hours of contact time (Figure 2.15).

To investigate bisphenol chloramination, a mixed bisphenol solution (with 20 µg/L each of BPA, BPD, BPB, BPE, and BPF) was spiked with monochloramine at 8 mg/L as Cl_2 (the control was the same mixed bisphenol solution with no monochloramine added). Measureable decay of the bisphenols did not occur until 7 hours of contact time (Figure 2.16), thus, bisphenols reacted with monochloramine much more slowly than with free chlorine.

All of the bisphenols demonstrated similar reactivity with both free chlorine and monochloramine. For this reason, and also because the chlorine demand associated with additional bisphenols would have made it more difficult to maintain acceptable pseudo-first-order test conditions (i.e., nearly constant chlorine concentration), only BPA and BPF were investigated in greater depth and used to develop a chlorination model (Chapter 5). BPF was

selected as the second representative bisphenol, in addition to BPA, as it is the second most reported bisphenol in environmental samples (and BPA is the most reported).[58,59]

2.3.2.2 Comparison of BPA Chlorination Data to Published Kinetic Data

Gallard *et. al.* developed a kinetic model for the chlorination of bisphenol A.[60] To see if similar results were being obtained in this study, three more preliminary experiments were conducted under conditions (pH, initial reactant concentrations, and temperature) mimicking the experiments reported by Gallard *et. al.*[60] Pseudo-first-order kinetic plots were constructed to compare results of this study with those of Gallard *e.t al.*[60] Figure 2.17 A shows the results of this study for the reaction of 1 µM BPA with 35 µM free chlorine ($HOCl/OCl^-$) at three pH values. The straight lines verify that a pseudo-first-order kinetic model was appropriate for these conditions. In Figure 2.17 B, the data presented in Figure 1 of the Gallard *et. al.*[60] paper were overlaid onto the experimental data from this study. The results were very similar for pH 6.7 and 8.2 but differed by a factor of about 2 for pH 10.3. The differences in the results at pH 10.3 were subsequently addressed in a thorough investigation of BPA chlorination (Chapter 5).

2.3.2.3 Formation of Chlorinated BPA By-products

After the rates of reaction of BPA with free chlorine and MCA had been experimentally established and found to be relevant for conditions applicable to water service lines, the focus of this aspect of the study shifted to chlorinated by-products of BPA reported in the literature (e.g., BPA-Cl, BPA-2Cl, BPA-3Cl, BPA-4Cl).[38,37] MS Q1 Scans were performed on a solution spiked with 2.2 µM (500 µg/L) BPA and 2.2 µM sodium hypochlorite (producing an initial free chlorine concentration of 0.8 mg/L as Cl_2). Key chlorination ions were tracked over time and showed a steady decay of BPA, followed by formation of the aforementioned chlorinated by-

products (Figure 2.18). A longer overall reaction time would be needed to identify the terminal end product(s).

2.3.2.4 Chlorination and Monochloramination of BADGE

BADGE has known chlorination products (e.g., BADGE-HCl, BADGE-2HCl, and BADGE-H_2O-HCl) but there is no evidence to suggest they form under drinking water treatment or distribution conditions. Research has focused on their detection in canned foods.[41,42] When analyzing solutions of BADGE, there is added complexity as BADGE is susceptible to hydrolysis and forms two hydrolysis products: BADGE-H_2O and BADGE-$2H_2O$.[61] The repercussion is that standards of BADGE, left at room temperature, form hydrolysis products within hours, meaning that the standard then contains BADGE, BADGE-H_2O, and BADGE-$2H_2O$. Chapter 4 will address hydrolysis in more detail. When investigating the chlorination of BADGE, the hydrolysis products were also monitored, in both the control and chlorinated samples, so that any effect of chlorination on the hydrolysis products could also be observed.

To investigate BADGE chlorination, solutions having a free chlorine residual of 1.9 mg/L as Cl_2 were adjusted to pH 7.6 and 9.0 (buffered with 5 mM phosphate) and spiked with BADGE, producing a nominal initial BADGE concentration of 200 µg/L (nominal because the BADGE began to hydrolyze when the spiking solution was prepared). A solution with a free chlorine residual of 1.9 mg/L as Cl_2 served as the chlorine control and a solution with nominal initial BADGE concentration of 200 µg/L was the analyte control. These solutions and two control solutions adjusted to the same pH values but with no chlorine added, were then analyzed over time for BADGE, BADGE-HCl, BADGE-2HCl, BADGE-H_2O-HCl, BADGE-H_2O and BADGE-$2H_2O$. The decay of BADGE in the chlorinated samples was very similar to its decay in

the control (Figure 2.19) and differences between the chlorinated samples and controls were not significant ($\alpha \leq 0.05$, ANOVA Test of Repeated Measures). Formation of hydrolysis by-products in the chlorinated samples was similar to that in the controls and no chlorinated by-products were detected. Lack of significant BADGE decay and lack of chlorinated by-products indicates that BADGE is not susceptible to chlorination under drinking water conditions.

Similar experiments were conducted to examine chloramination of BADGE. Specifically MCA solutions having a combine chlorine residual of 3.5 mg/L as Cl_2 were adjusted to pH 7.6 and 9.0 (buffered with 5 mM phosphate) and spiked with BADGE, producing a nominal initial BADGE concentration of a 200 µg/L BADGE. A solution with a combine chlorine residual of 3.5 mg/L as Cl_2 served as the chlorine control and a solution with nominal initial BADGE concentration of 200 µg/L was the analyte control. At both pH values, decay of BADGE in the chlorinated samples was very similar to that observed in the controls (Figure 2.20) and the differences were not statistically significant ($\alpha \leq 0.05$, ANOVA Test of Repeated Measures). Chlorinated by-products of BADGE and BADGE hydrolysis products were not detected at either pH value. Lack of significant BADGE decay and lack of chlorinated by-products suggests BADGE is not susceptible to chloramination under drinking water conditions.

MCA appeared to be influencing BADGE hydrolysis (Figure 2.20). At pH 7.6, the hydrolysis products appeared to be forming much more rapidly in the presence of MCA; however, this may be an analytical artifact, as there was no corresponding increase in BADGE decay. At pH 9, the BADGE concentration appeared to increase slightly, but significantly, during the first two days of contact with MCA (Figure 2.20). This experiment was repeated twice, and in both cases an apparent increase in the BADGE concentration at two days of contact time was

again observed (Figure 2.21). The reproducibility of this unexpected result suggests that it may be due to a matrix effect in the electrospray, that is, one or more species present in the two day samples at a different concentration than on other days could be causing an electrospray enhancement. Although these apparent artifacts were of interest analytically, the additional work that would be required to fully elucidate the reasons for them could not be justified when taking into consideration the project's primary objectives.

2.3.3 End-Fitting Leaching and Adsorption for Fill-and-Dump Experiments

During fill-and-dump experiments, the fill solutions would be exposed to various surfaces, including the uncoated copper or lead pipes (controls), to the lining or coating, and to end-fittings components. Due to frequent reported analytical contamination from BPA and phthalates, the end-fittings were evaluated for bisphenol and phthalate leaching, and also for adsorption of these analytes (potentially leading to reduced concentrations or false non-detections). The end-fitting components included stoppers (silicone and HDPE) and stainless steel (SS) and HDPE pipe nipples (Figure 2.8).

2.3.3.1 End-Fitting Leaching and Adsorption of Bisphenols

A preliminary investigation of the bisphenol standards in contact with silicone stoppers resulted in minimal adsorption (Figure 2.22 A). The two multi-component end-fitting assemblages (Figure 2.8) were used to test bisphenol leaching and adsorption and resulted in no leaching or adsorption after 24 hours (Figure 2.22 B and C). Based on this data, silicone stoppers and all end-fittings were considered acceptable for contact with bisphenol samples.

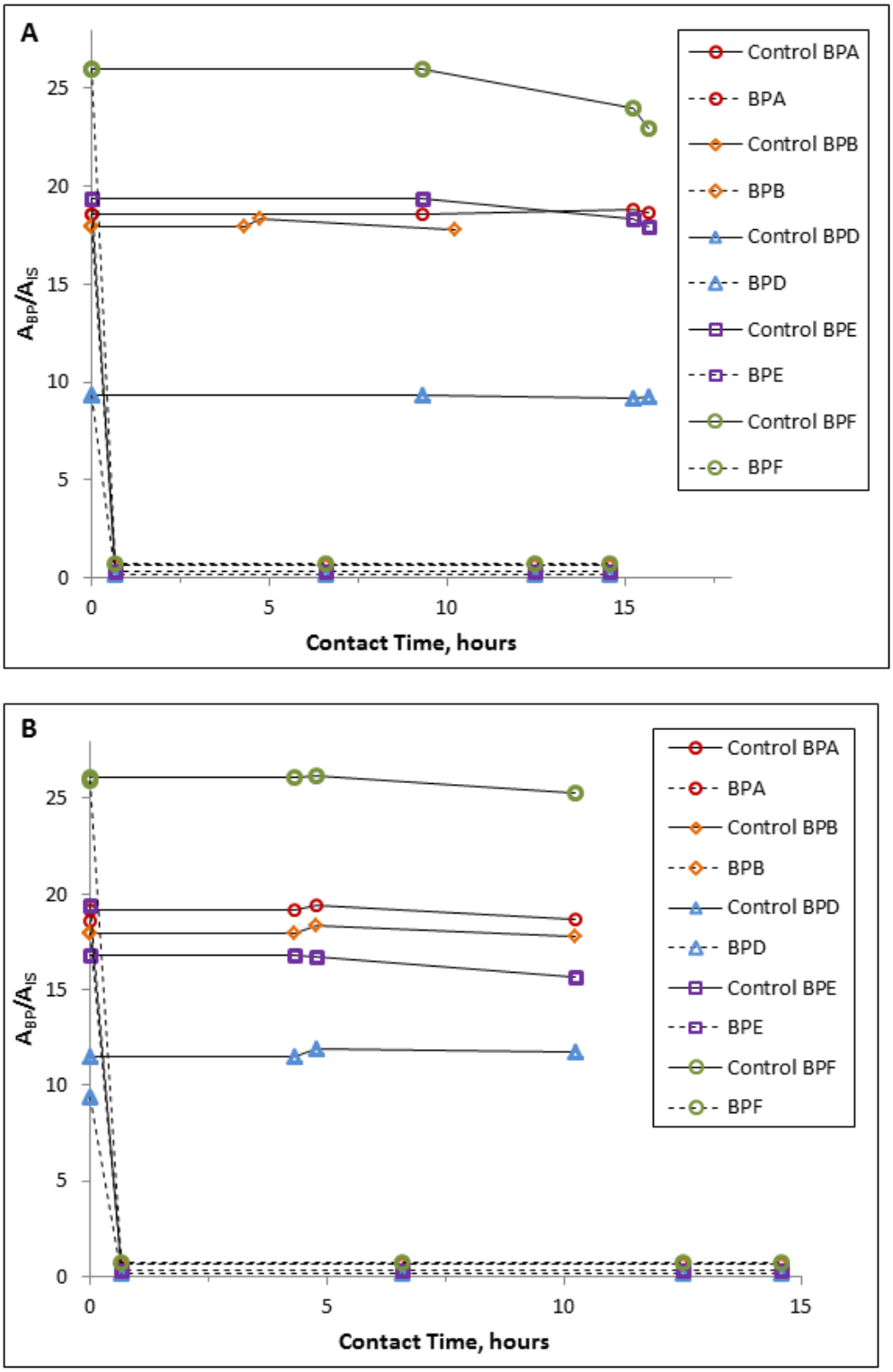


Figure 2.14 Stability of bisphenols over time with exposure to free chlorine at 2 mg/L as Cl_2 at pH 9.6 (A) and 7.6 (B). Controls are bisphenol standards with no chlorine.

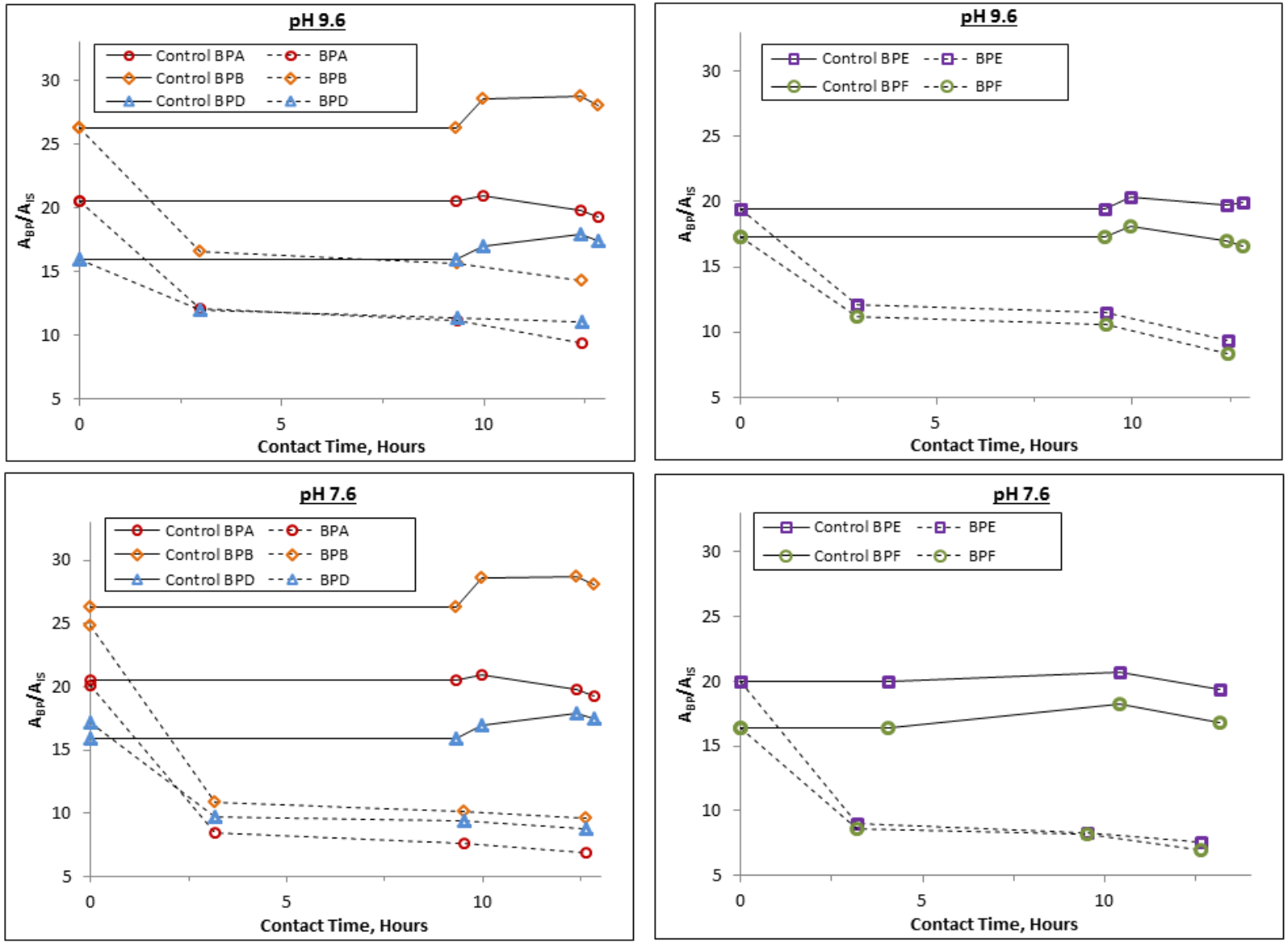


Figure 2.15 Stability of bisphenols over time with exposure to free chlorine at 0.2 mg/L as Cl_2. Controls are bisphenol standards with no chlorine.

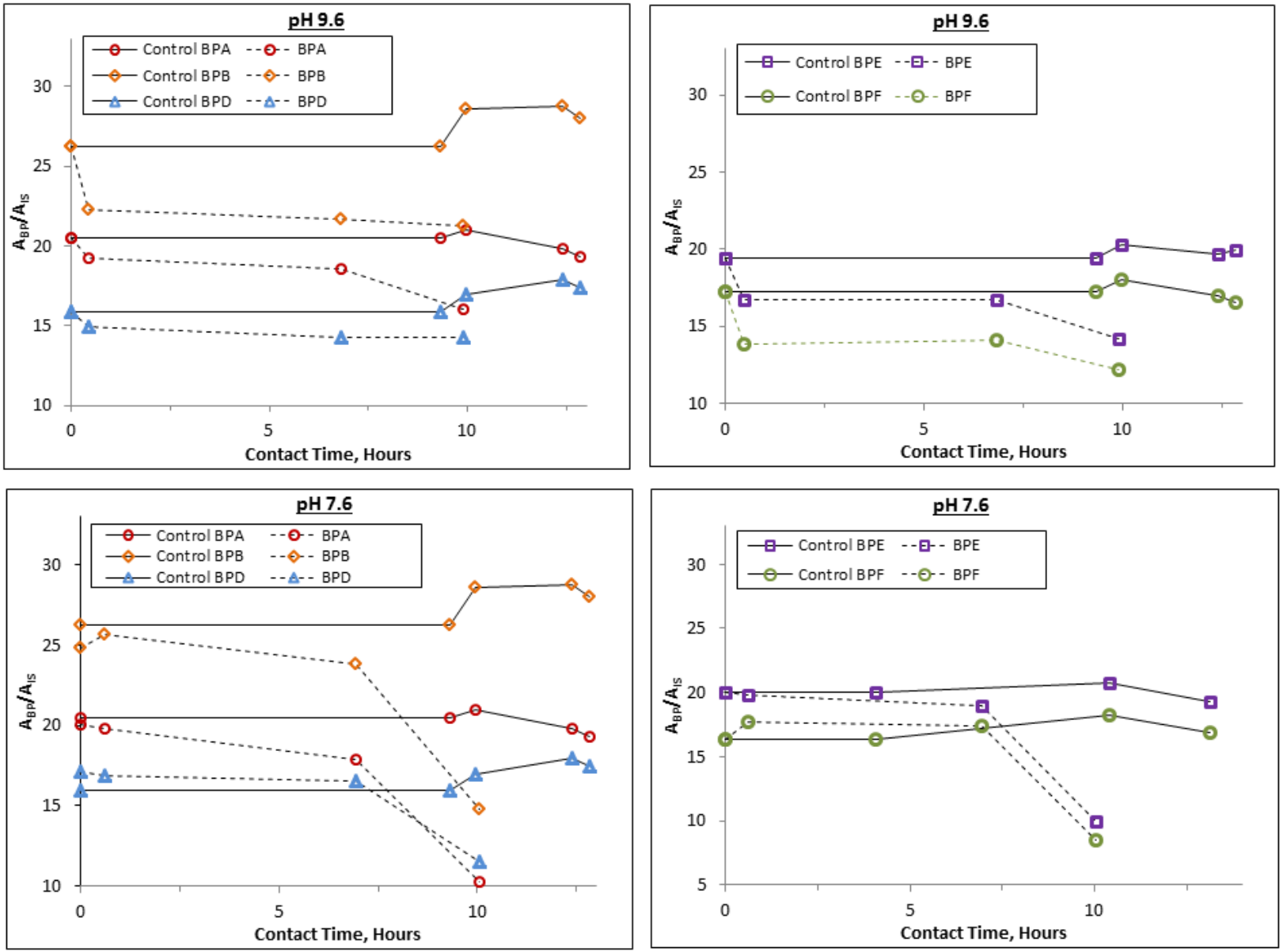


Figure 2.16 Stability of bisphenols over time with exposure to monochloramine at 8 mg/L as Cl_2. Controls are bisphenol standards with no chlorine.

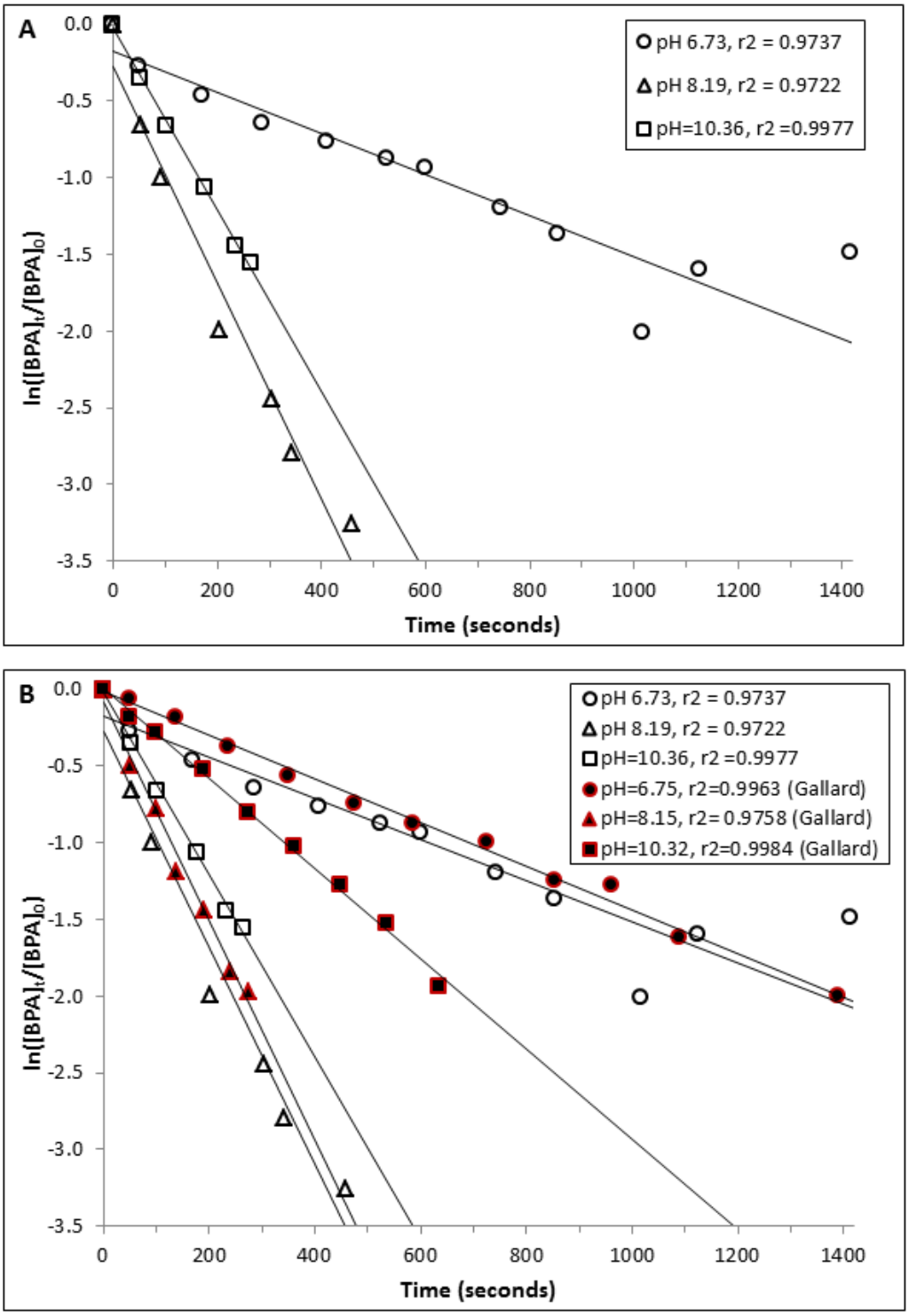


Figure 2.17 Pseudo-first-order decay of BPA at various pH values for an initial BPA concentration of 1 µM and an initial free chlorine concentration of 35 µM. (A) Experimentally determined values (B) Experimentally determined values with an overlay of data from Gallard *et. al.*[60]

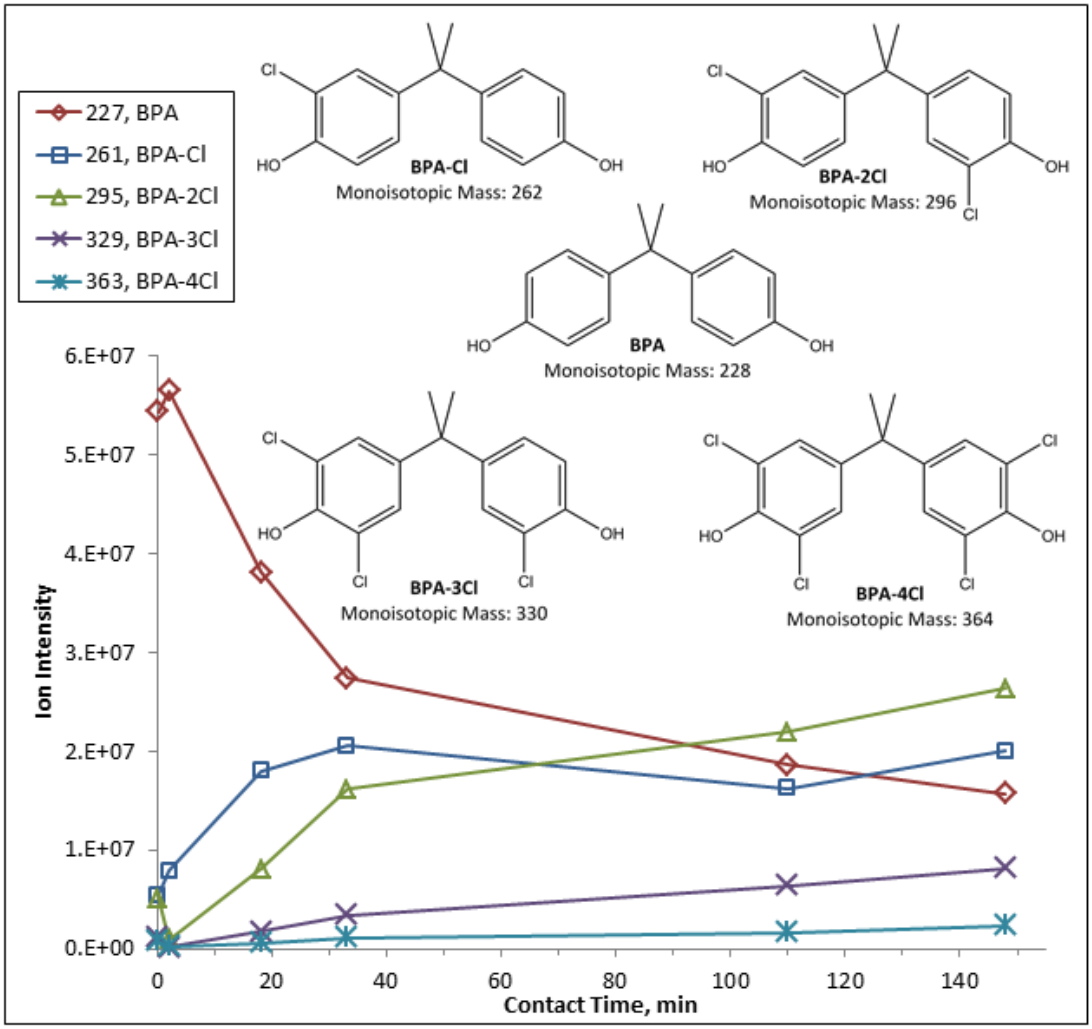


Figure 2.18 MS ion scans tracking of BPA and chlorinated BPA by-products for an initial BPA concentration of 500 µg/L (2.2µM) and an initial free chlorine concentration of 0.8 mg/L as Cl_2 (2.2µM).

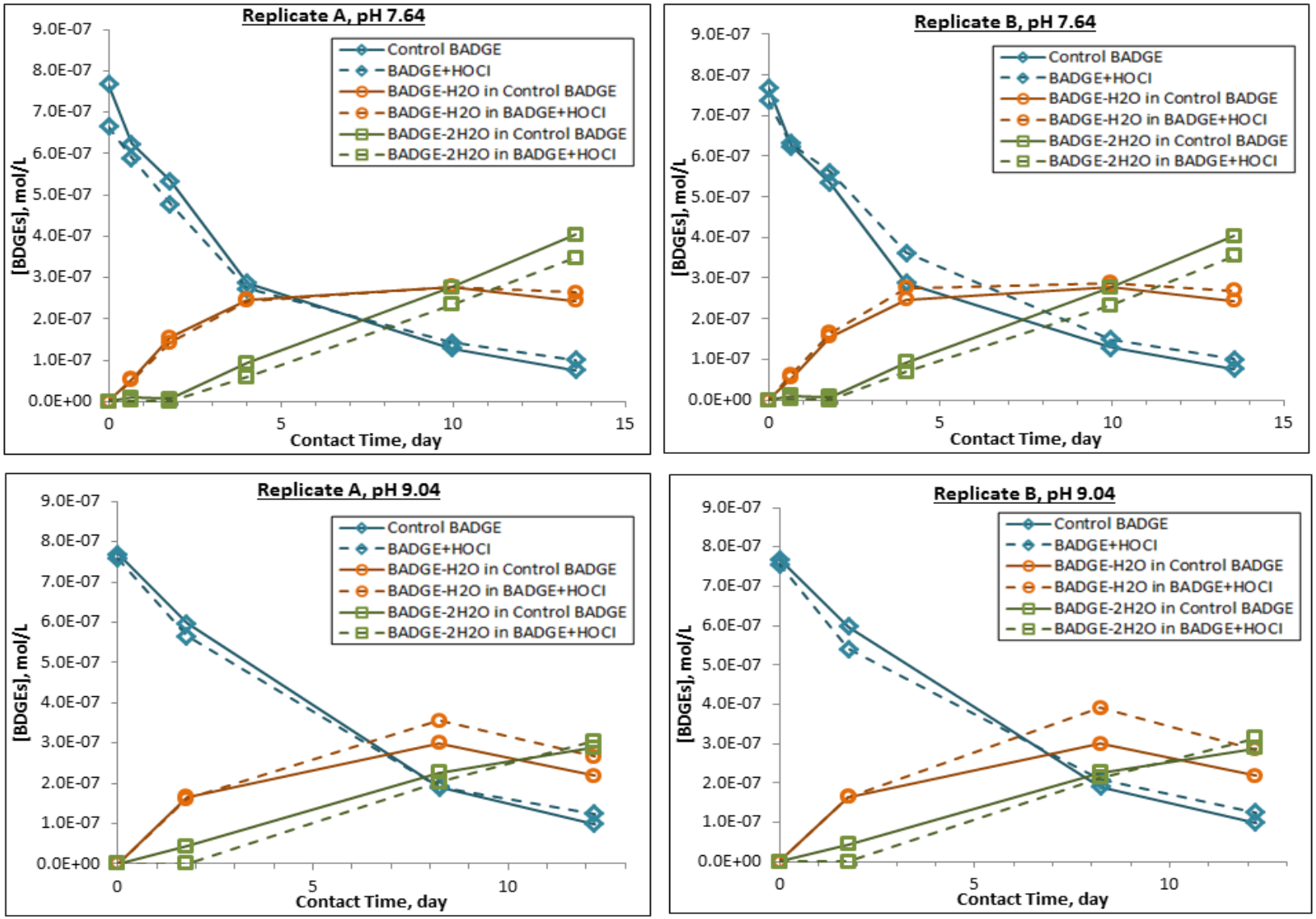


Figure 2.19 Chlorination of BADGE with free chlorine (1.9 mg/L as Cl_2) at pH 7.64 and 9.04. (The initial BADGE concentration was nominally 200 µg/L. The unchlorinated control samples are designated as "Control BADGE" and the chlorinated samples as "BADGE + HOCl.) BADGE-HCl, BADGE-2HCl, and BADGE-H_2O-HCl were not detected.

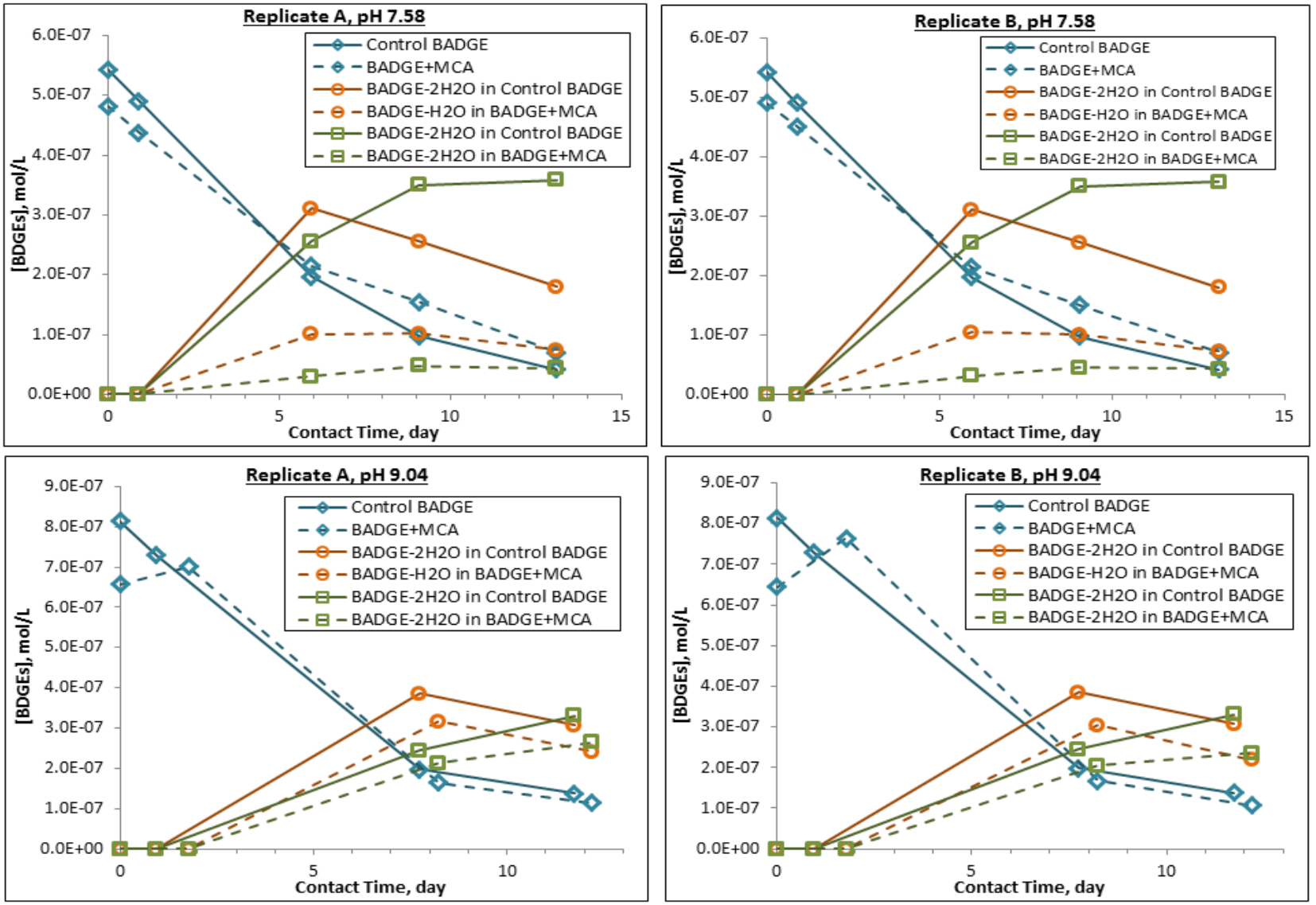


Figure 2.20 Chloramination of BADGE with MCA (3.5 mg/L as Cl_2) at pH 7.58 and 9.04. (The initial BADGE concentration was nominally 200 µg/L. The unchlorinated control samples are designated as "Control BADGE" and the chlorinated samples as "BADGE+MCA".) BADGE-HCl, BADGE-2HCl, and BADGE-H_2O-HCl were not detected.

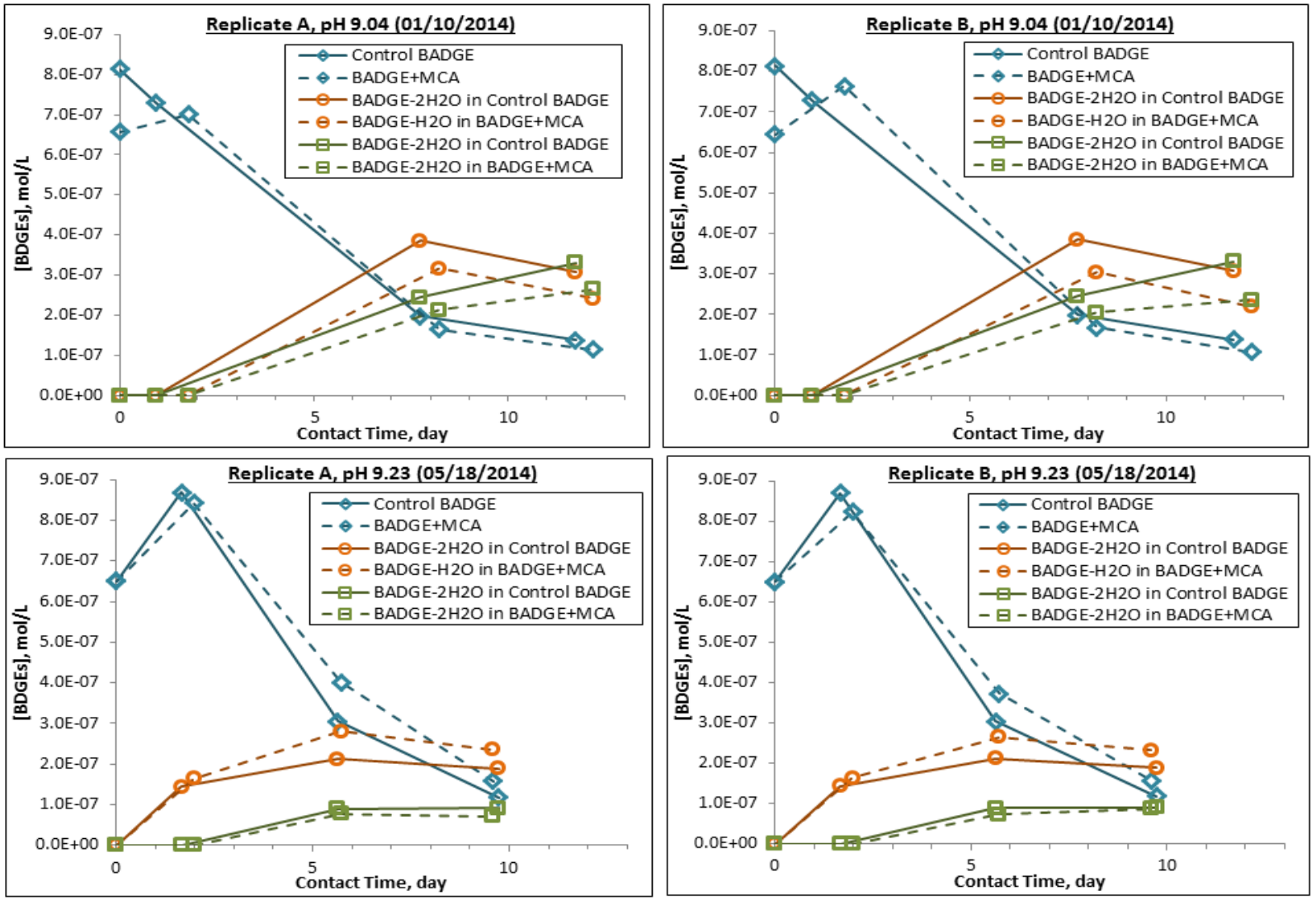


Figure 2.21 Chloramination of BADGE with MCA (3.5 mg/L as Cl_2) at pH 9. (The initial BADGE concentration was nominally 200 µg/L. The unchlorinated control samples are designated as "Control BADGE" and the chlorinated samples as "BADGE+MCA".

2.3.3.2 End-Fitting Leaching and Adsorption of BADGE

BADGE leaching and adsorption experiments were performed by testing the SS pipe nipples, threaded SS pipe nipples, and silicone stoppers individually. BADGE end-fitting leaching was not observed, even at the longest holding time (9.5 days). Minimal BADGE adsorption to the SS pipe nipples was observed (Figure 2.23); the decay over time is due to the hydrolysis of BADGE to by-products (BADGE-$2H_2O$ and BADGE-$2H_2O$). The silicone stoppers showed adsorption of BADGE after 6 hours, and adsorption of BADGE and it hydrolysis products at longer contact times (Figure 2.24A), albeit at an 11 times greater surface area-to-volume ratio than used in the fill-and-dump sampling. The adsorption study was repeated with a surface-to-volume ratio equivalent to fill-and-dump pipe sections (0.0158 cm^2/mL) and significant adsorption was still noted after 6 hours and longer contact times (Figure 2.24 B). Thus, avoidance of silicone stoppers is recommended for water samples to be analyzed for BADGE and its hydrolysis products. However, this was not yet recognized during the fill-and-dump experiments, and silicone stoppers were used on pipe sections from which samples were collected and analyzed for BADGE; hence the BADGE concentrations were most likely under-reported due to adsorption.

2.3.3.3 End-Fitting Leaching and Adsorption of Phthalate Esters (PAEs)

PAEs leaching and adsorption studies were conducted by testing unthreaded SS pipe nipples, threaded SS pipe nipples, silicone stoppers, and HDPE stoppers individually. PAE leaching was not observed, even at the longest holding time (7 days). SS pipes nipples showed significant adsorption (or, more likely, decay) of all the PAEs at 6 days (Figure 2.25) and three PAEs (DNOP, DEHA, and DEHP) at 20 hours. The silicone stoppers showed significant

adsorption of all PAEs at 20 hours (Figure 2.26 A), while the HDPE stopper exhibited little or no loss of PAEs after 18 hours and significantly adsorbed only 3 of the PAEs after 7 days (BBP, DEHA, DNBP) (Figure 2.26 B). Therefore, HDPE stoppers are recommended for use with PAE samples and avoidance of silicone stoppers and long-term contact with stainless steel is also recommended. The SS pipe nipples were considered adequate for PAE samples in the fill-and-dump leaching experiment for two reasons: 1) no PAEs were found leaching from the pipe nipples; and 2) had any PAEs leached from the PET liner, they would not have come into contact with the SS pipe nipples, since the lining extended through the pipe nipples.

2.3.3.4 End-Fitting Leaching and Adsorption of Phthalic Acids (PAs)

PA leaching and adsorption studies were conducted by testing the unthreaded SS pipe nipples, threaded SS pipe nipples, silicone stoppers, and HDPE stoppers individually. PA leaching was not observed, even at the longest 7 day holding time and little or no adsorption was observed (Figure 2.27). Thus, all of the end-fittings were compatible with samples to be analyzed for PAs.

2.3.4 Epoxy Coating Fill-and-Dump Experiments

2.3.4.1 Analysis of Epoxy Starting Material

Ingredients of the potable water grade epoxy were considered proprietary and not made available by the manufacturer. To anticipate key epoxy leachates, part A and part B of the starting materials were dissolved in methanol, diluted, and analyzed using GC/MS scan. A major key peak in part A was identified as BADGE using the National Institute of Standards and Technology (NIST) spectral library (chromatogram and mass spectrum provided in Chapter 4,

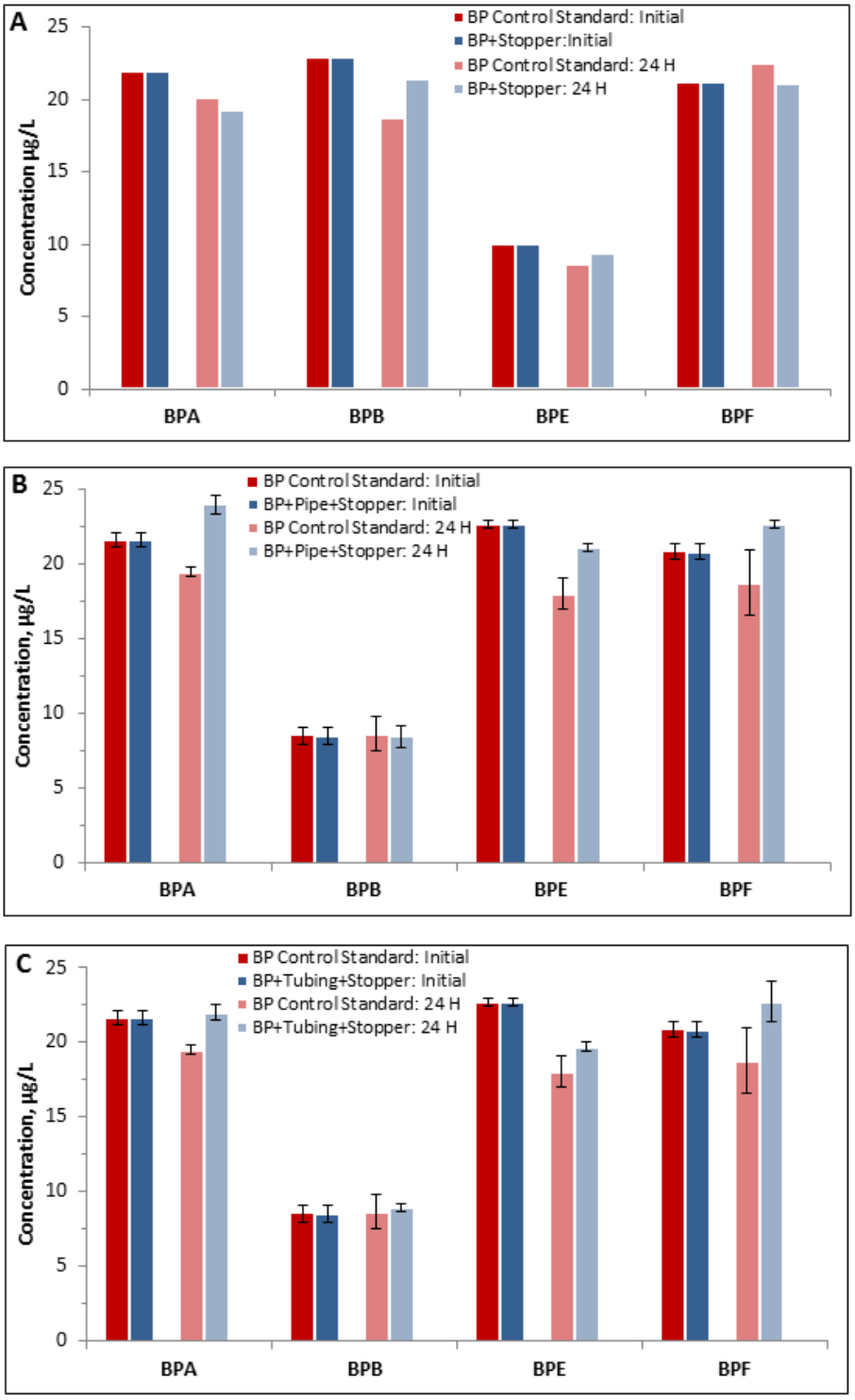


Figure 2.22 Bisphenol adsorption to end-fittings. A) Adsorption of bisphenols to silicone stoppers. B) Bisphenol adsorption to the multi-component SS assemblage. C) Bisphenol adsorption to the multi-component HDPE assemblage. Error bars are the standard deviations for n = 2 replicate samples.

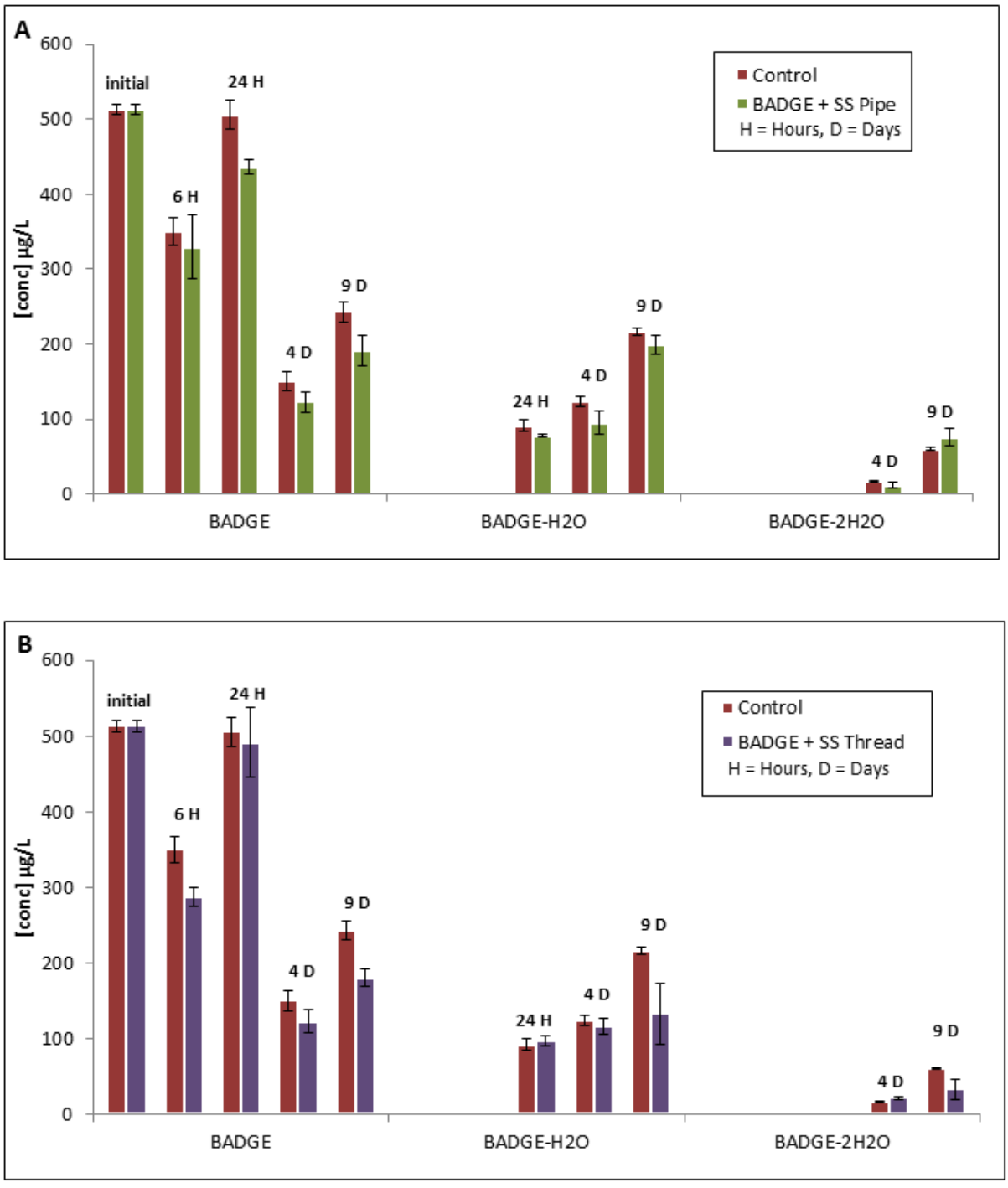


Figure 2.23 BADGE adsorption to SS pipe nipples and monitoring of BADGE hydrolysis by-product formation. A) Adsorption of BADGE to unthreaded SS pipe nipple. B) Adsorption of BADGE to threaded SS pipe nipple. Error bars are the standard deviations for n = 3 replicate samples.

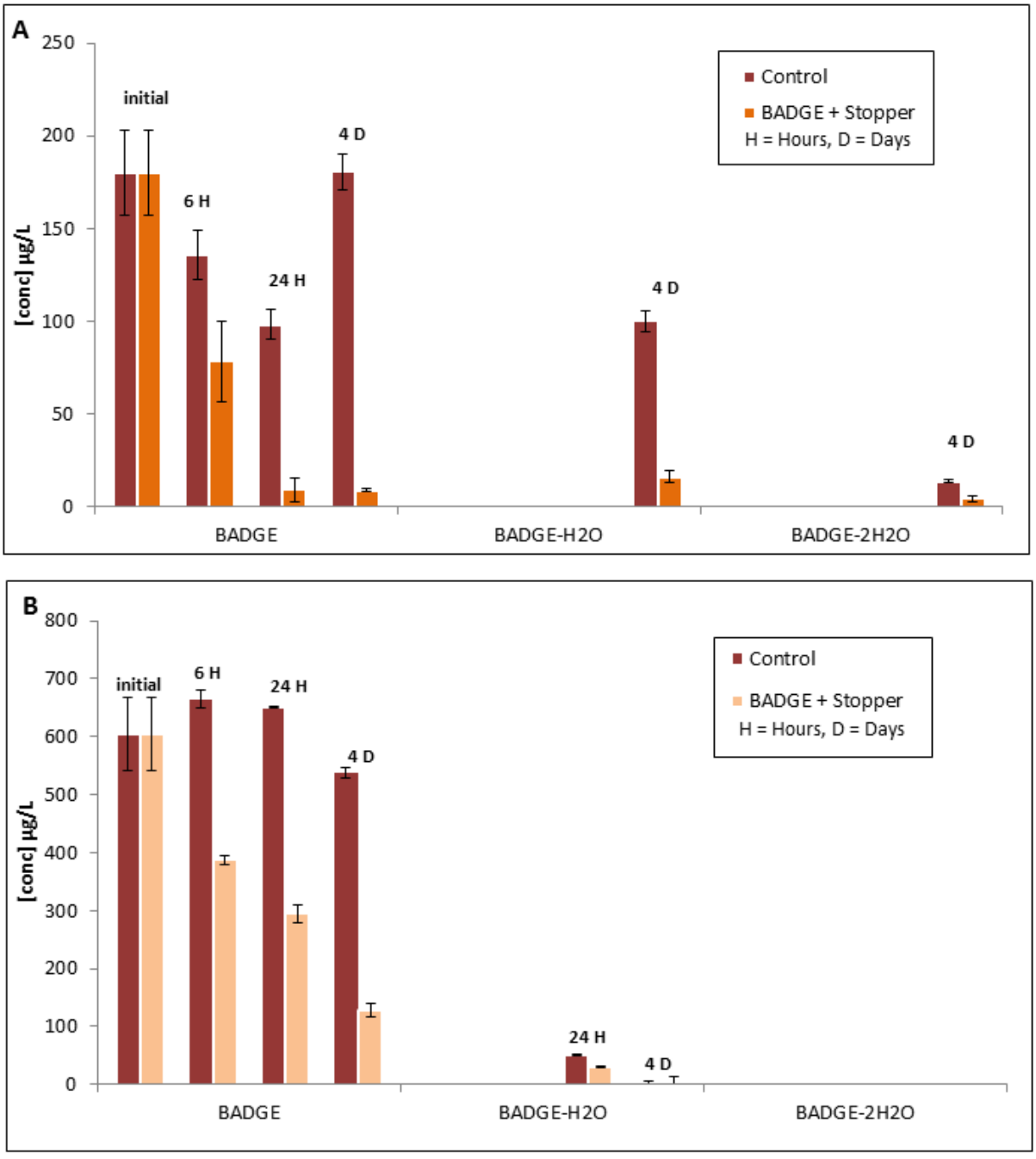


Figure 2.24 BADGE adsorption to silicone stoppers and monitoring of BADGE hydrolysis by-product formation. A) Adsorption of BADGE to silicone stopper with a surface area-to-volume ratio of 0.175 cm^2/mL. B) Adsorption of BADGE to silicone stopper with a surface area-to-volume ratio of 0.0158 cm^2/mL. Error bars are the standard deviations for n = 3 replicate samples.

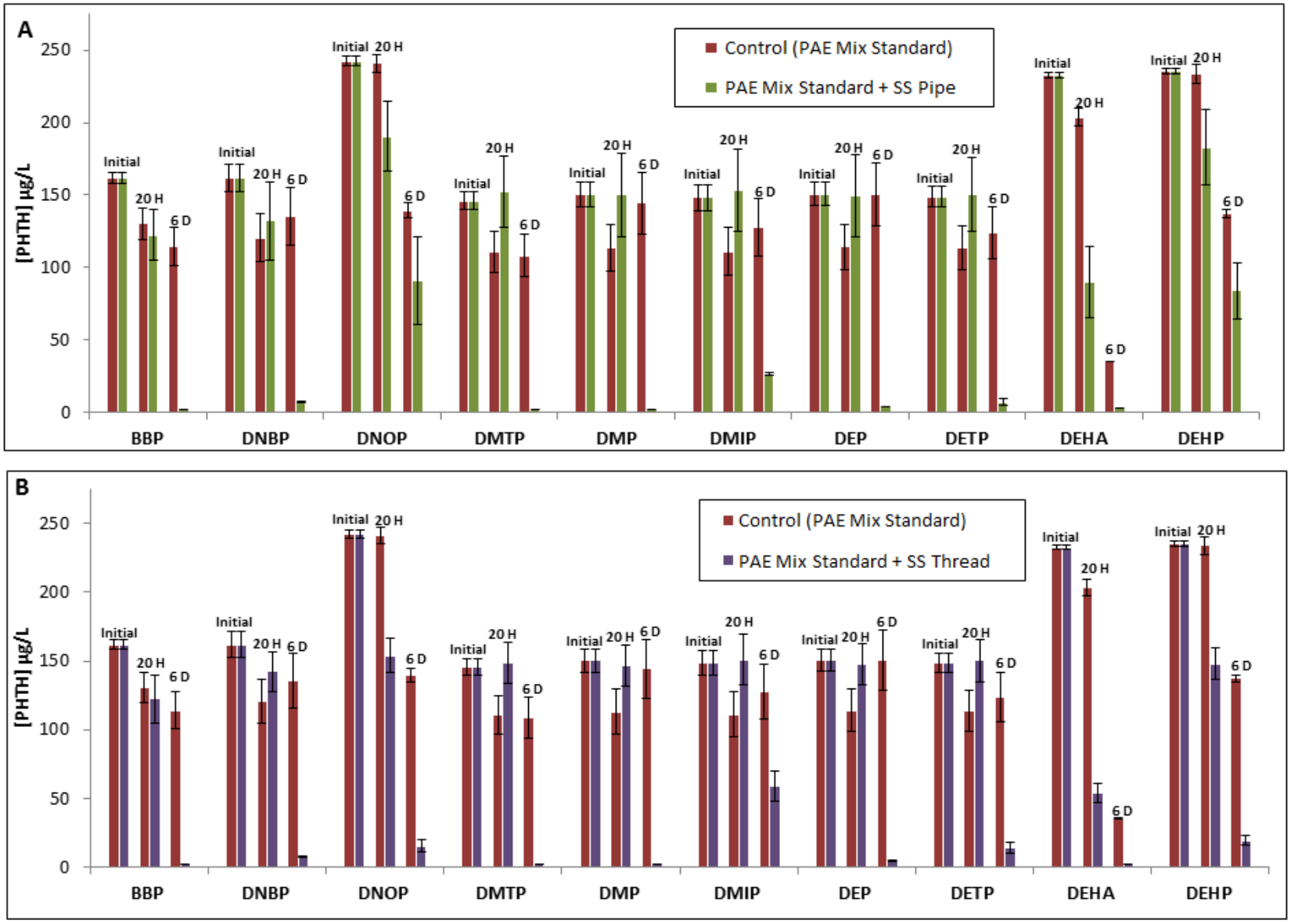


Figure 2.25 PAEs adsorption to SS pipe nipples. A) Adsorption of PAEs to unthreaded SS pipe nipples. B) Adsorption of PAEs to threaded SS pipe nipples. Error bars are the standard deviations for n = 3 replicate samples.

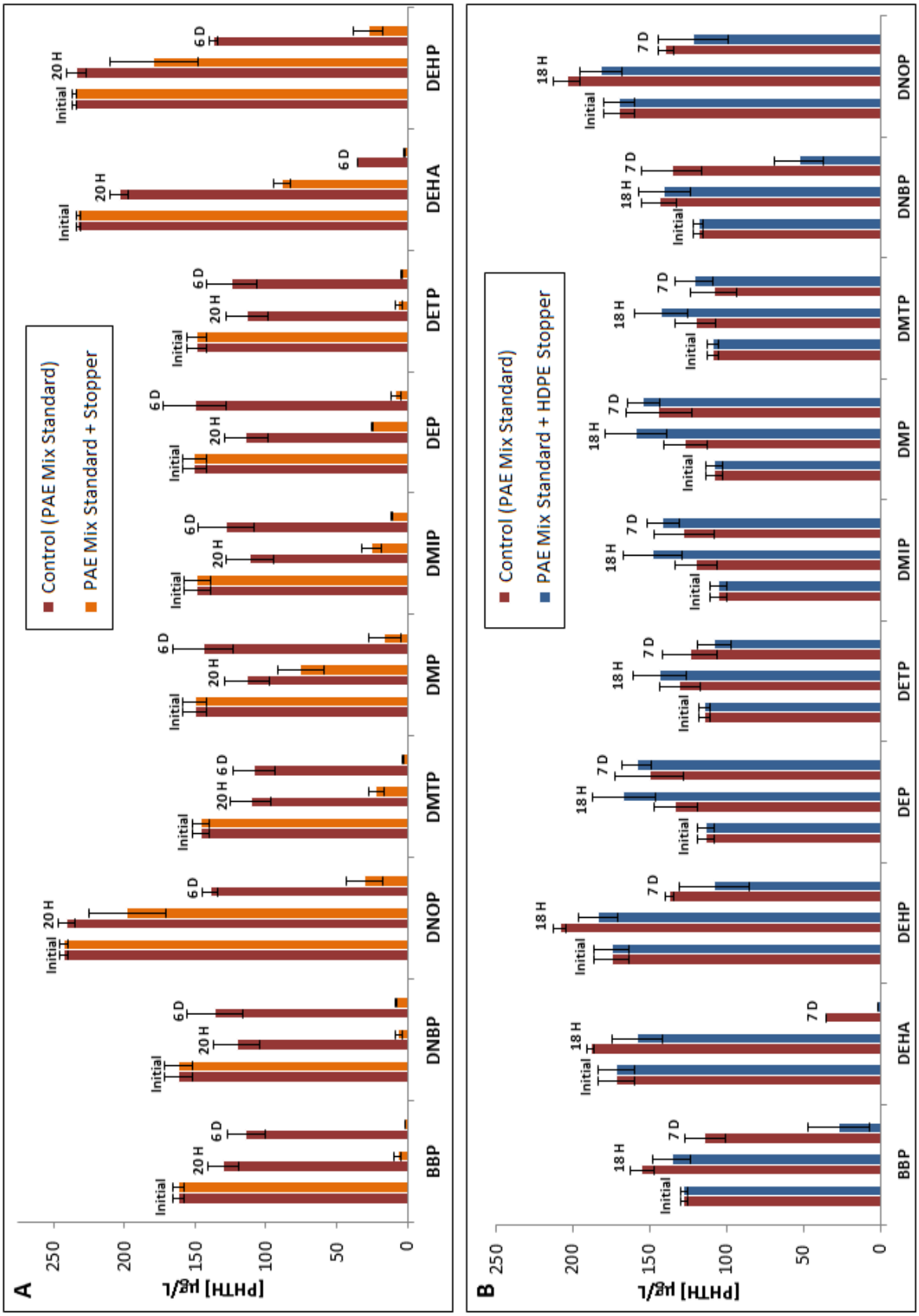


Figure 2.26 PAE adsorption to stoppers. A) Adsorption of PAEs to silicone stopper. B) Adsorption of PAEs to HDPE stopper. Error bars are the standard deviations for n = 3 replicate samples.

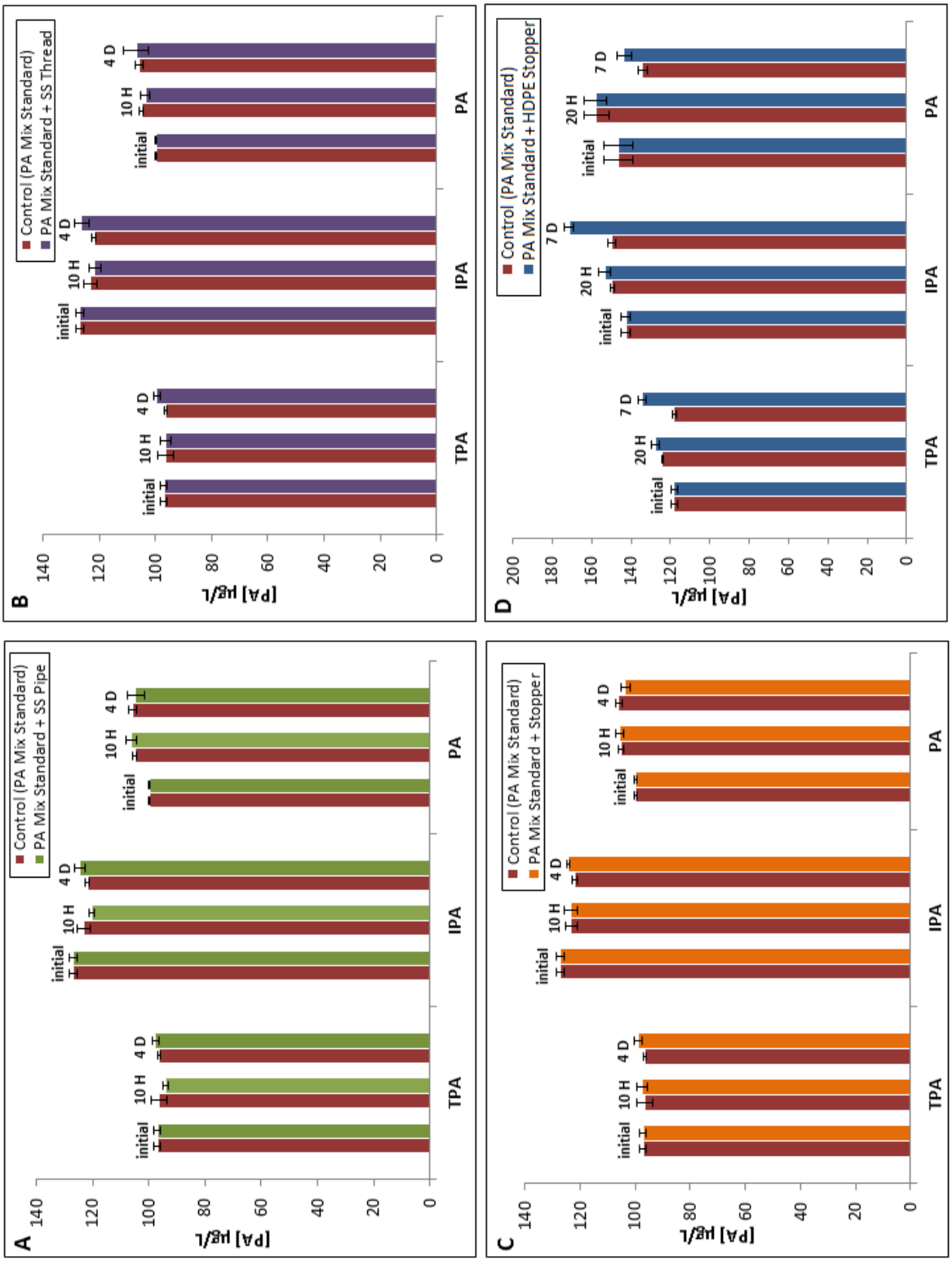


Figure 2.27 PA adsorption to end-fittings. (A) Unthreaded SS pipe nipples. (B) Threaded SS pipe nipples. (C) Silicone stopper. (D) HDPE stopper. Error bars are the standard deviations for n = 3 replicate samples.

Figure 4.2). Other potential starting materials, bisphenols (i.e., BPA, BPB, BPD, BPE, BPF, BPS) or BFDGE, were not detected in the epoxy formulation studied.

2.3.4.2 First Epoxy Coating Fill-and-Dump Experiment (FD1)

Results from the first fill-and-dump epoxy coating experiment (FD1) are shown in Table 2.8. BADGE was detected at shorter holding times in 9 of the 36 samples and ranged from 13 to 340 µg/L. The lack of BADGE at longer holding times was attributed to hydrolysis (and adsorption to the silicone stoppers, Section 2.3.3.2) and BADGE hydrolysis is explored in detail in Chapter 4. BPA was only detected in 5 of the 36 samples and ranged from 0.25 to 1.7 µg/L. Other compounds were noted in the samples which had ions with the same MS/MS quantitation and confirmation ions as BPA but different retention times. These unknown compounds eluted at 6.0 and 6.4 min as opposed to the 6.6 min retention time for BPA (Figure 2.28). BPA-like compounds were detected in 31 of the 36 samples and ranged from 0.94 to 94 µg/L. To eliminate the possibility that sample matrix affects were shifting the retention time of BPA, selected samples were spiked with a BPA standard and BPA eluted at 6.5 min (Figure 2.28). All matrix spike results are presented in Appendix A.1.11. These unknown compounds were termed “BPA-like” and are discussed in greater detail in Chapter 3. Samples were also analyzed for BPB, BPD, BPE, BPF, and BPA-4Cl but all of these were undetected.

Total chlorine concentrations in the chlorinated pH 8 extraction water were monitored before and after pipe holding times and the epoxy coatings were found to significantly remove chlorine from solution (Table 2.9). After 24 hours of epoxy exposure, the chlorine concentration decreased by 95%, whereas chlorinated extraction water held in an amber glass bottle showed

Table 2.8 BADGE, BPA, and BPA-like compounds detected in extraction waters of the first epoxy-coating fill-and-dump experiment (FD1).

Extraction Water and Holding Time	BADGE, µg/L		BPA, µg/L		BPA-like, µg/L* 6.0 min RT		BPA-like, µg/L* 6.4 min RT	
	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs
Dechlorinated pH 8 Tap Water	≤7.0	≤7.0	≤0.057	≤0.057	ND	ND	ND	ND
Control (unlined) – 6 h	≤7.0	≤7.0	≤0.057	≤0.057	0.94	ND	ND	ND
6 h (A)	340	32	≤0.057	≤0.057	36	52	ND	ND
6 h (B)	214	36	≤0.057	≤0.057	49	62	ND	ND
24 h	241	≤7.0	≤0.057	≤0.057	34	46	ND	ND
4 d	≤7.0	≤7.0	≤0.057	≤0.057	68	54	5.6	6.3
24 h, then 10 d	≤7.0	≤7.0	≤0.057	≤0.057	10	14	3.3	11
Chlorinated pH 8 Extraction Water	≤7.0	≤7.0	≤0.057	≤0.057	ND	ND	ND	ND
6 h	236	76	≤0.057	≤0.057	37	7.4	9.4	ND
24 h	101	≤7.0	≤0.057	≤0.057	51	59	12	13
4 d	≤7.0	≤7.0	≤0.057	≤0.057	94	20	20	11
24 h, then 10 d	≤7.0	≤7.0	≤0.057	1.7	ND	11	51	23
pH 6.5 Extraction Water	≤7.0	≤7.0	≤0.057	≤0.057	ND	ND	ND	ND
Control (unlined) initially filled with dechlorinated pH 8 tap water, held for 6 h, then								
6 h	≤7.0	≤7.0	≤0.057	≤0.057	ND	ND	ND	ND
6 h, then 7 d	≤7.0	≤7.0	≤0.057	≤0.057	ND	ND	ND	ND
Pipes initially filled with dechlorinated pH 8 tap water, held 6 h, then:								
6 h (A)	≤7.0	≤7.0	≤0.057	≤0.057	11	14	ND	ND
6 h (B)	≤7.0	≤7.0	0.82	≤0.057	7.4	11	2.5	1.7
6 h, then 7 d (A)	≤7.0	≤7.0	0.25	≤0.057	16	8.8	11	10
6 h, then 7 d (B)	≤7.0	≤7.0	≤0.057	≤0.057	15	13	7.8	6.3
Pipes initially filled with chlorinated pH 8 extraction water, held 6 h, then:								
6 h	13	≤7.0	1.3	≤0.057	9.0	8.2	4.0	5.1
6 h, then 7 d	≤7.0	≤7.0	1.6	≤0.057	ND	11	12	13

* Assuming a response factor equivalent to BPA ND = not detected LSLs = Lead service lines
CSLs = Copper service lines

Table 2.9 Residual chlorine* data for epoxy-coated pipe sections in FD1.

Extraction Water and Holding Time	Residual Cl_2, mg/L as Cl_2	
	LSLs	CSLs
Dechlorinated pH 8 Tap Water	≤ 0.02	≤ 0.02
Chlorinated pH 8 Extraction Water (control = 0 h)	2.00	2.00
Chlorinated pH 8 Extraction Water (control = 6 h)	1.93	1.93
6 h	0.17	0.33
24 h	0.08	0.12
4 d	≤ 0.02	≤ 0.02
24 h, then 10 d	≤ 0.02	≤ 0.02

LSLs = Lead service lines CSLs = Copper service lines
*Measured with the HACH Total Chlorine Method 8167; selected samples were spot tested to verify the absence of combined chlorine.

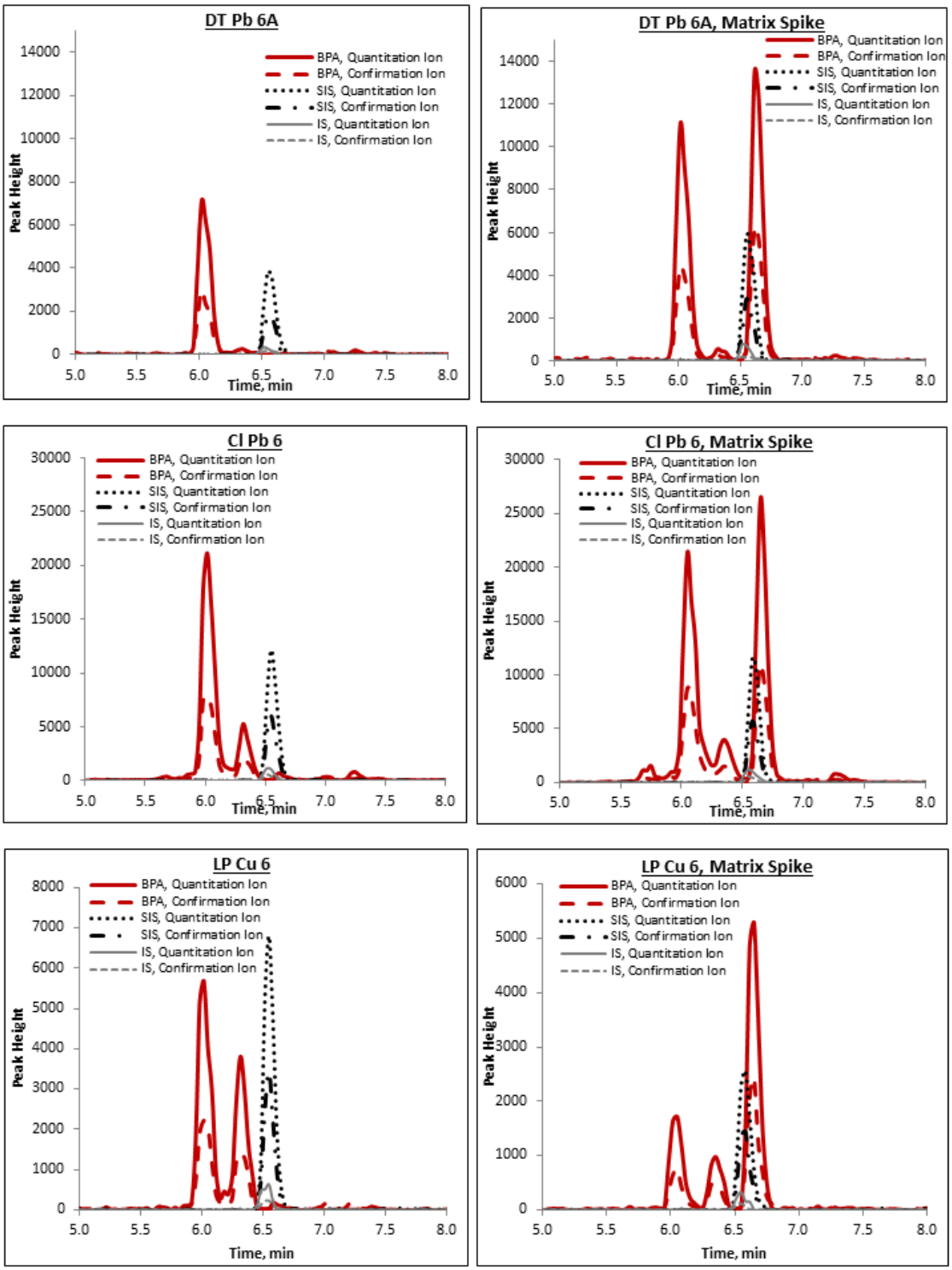


Figure 2.28 Selected samples from FD1 with a BPA-like compound present before and after the addition of a 40 µg/L BPA standard matrix spike. DT-Pb-6A was from an epoxy-coated LSL section filled with dechlorinated pH 8 tap water and held for 6 hours. CL-Pb-6 was from an epoxy-coated LSL section filled with chlorinated pH 8 extraction water and held for 6 hours. LP-Cu-6 was from an epoxy-coated CSL section filled with pH 6.5 extraction water and held for 6 hours.

only a 4% decrease in chlorine concentration. Chlorine removal has been noted in other drinking water studies but the mechanism of removal is unknown.[62] Because chlorine is a key disinfecting agent in drinking water distributions systems, its reaction with the epoxy coating is an important result. This reaction has implications for chlorine residuals at the tap, for biological growths in the service line, and for disinfection by-product formation. Additionally, chlorine could prematurely age an epoxy lining, shortening its service life. Breault[55] explored the chlorination of this epoxy coating in more detail.

2.3.4.3 Second Epoxy Coating Fill-and-Dump Experiment (FD2)

The second fill-and-dump experiment addressed how storage conditions affect leaching of the key organic constituents. Table 2.6 shows the pipe section use history in FD1 and FD2. Of particular interest is that, for both the LSL and CSL pipe sections, Pipe02 was stored wet, Pipe08 was exposed to chlorinated pH 8 extraction water in FD1, and Pipe09 was not used in FD1. In FD2, BADGE was not detected, but BADGE hydrolysis by-products, BPA, and BPA-like compounds were detected, as described below. Matrix spikes during FD2 showed a similar result as FD1 in that the BPA-like compounds were not an artifact of a matrix effect (Appendix A.1.12).

The concentrations of BADGE and its hydrolysis by-products found in the extraction waters are summarized in Table 2.10. BADGE was a not detected but hydrolysis products were: BADGE-H_2O was detected in 2 of the 38 samples, ranging from 3.2 to 4.6 µg/L and BADGE-$2H_2O$ in 23 of the 38, ranging from 0.83 to 91 µg/L. An unknown compound was detected that eluted 3 minutes earlier than BADGE-H_2O (Figure 2.29) and had quantitation and confirmation ion intensities that were inverted compared to those of BADGE-H_2O. This compound was detected

in 32 of the 38 samples, and because the structure is unknown, its response factor was reported along with an estimated concentration range from 1.1 to 98 µg/L that assumes a response equivalent to that of BADGE-H2O (Table 2.11).

In FD2, BPA was detected in 35 of the 38 samples and ranged from 0.22 to 12 µg/L (Table 2.12). In addition to the BPA-like compounds at 6.0 and 6.4 min, there were additional BPA-like compounds detected at 4.4, 5.7, 5.9, and 7.4 min. BPA-like compounds with retention times from 6.0 to 6.4 min were noted in all of the samples, with concentrations ranging from 4 to 194 µg/L. BPA-like compounds with retention times from 4.5 to 5.9 min (Figure 2.30) were observed in all the 38 samples and ranged from 0.17 to 60 µg/L. The BPA-like compounds are addressed in greater detail in Chapter 3.

In general, for the BADGE, BPA, and BPA-like compounds, Pipe08 (exposed to chlorinated extraction water in FD1) and Pipe09 (not used in FD1) leached slightly higher levels. Storing an epoxy-coated pipe section wet as opposed to dry did not have a noticeable impact on the leached analytes.

Residual chlorine concentrations in the chlorinated extraction water and samples from the FD2 pipe sections are summarized in Table 2.13. Despite the epoxy coatings having aged during storage, they still removed 73 to 99% of the starting chlorine concentration. The propensity of the epoxy coating to react with chlorine and the slightly higher concentrations of leached organics in the chlorinated pH 8 extraction water indicates that chlorine does affect the epoxy coating.

Table 2.10 BADGE and BADGE hydrolysis by-products detected in extraction waters of the second epoxy-coating fill-and-dump experiment (FD2).

Extraction Water and Holding Time	BADGE, µg/L		BADGE-H_2O, µg/L		BADGE-$2H_2O$, µg/L	
	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs
Chlorinated pH 8 Extraction Water (0 h)	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe08: 6 h	≤ 7.0	≤ 7.0	4.6	≤ 1.0	91	2.2
Pipe02: 24 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	1.8	0.83
Pipe05: 24 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	3.5	11
Pipe09: 24 h	≤ 7.0	≤ 7.0	3.2	≤ 1.0	231	≤ 1.0
Chlorinated pH 8 Extraction Water (0 h)	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe02: 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe05: 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	2.5	6.3
Pipe09: 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	66	46
Reflushed, then:						
Chlorinated pH 8 Extraction Water (0 h)	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe02: 6 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe05: 6 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe08: 6 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	38	6.7
Pipe09: 6 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	2.8
Chlorinated pH 8 Extraction Water (0 h)	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe02: 6 h, then 24 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe05: 6 h, then 24 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe08: 6 h, then 24 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	19	2.0
Pipe09: 6 h, then 24 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	1.9	≤ 1.0
Chlorinated pH 8 Extraction Water (0 h)	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe02: 6 h, then 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe05: 6 h, then 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	1.1	1.5
Pipe08: 6 h, then 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	21	5.4
Pipe09: 6 h, then 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	6.5	5.8

Pipe08 was exposed to chlorinated extraction water in FD1, Pipe02 was stored wet, and Pipe09 was not used in FD1.

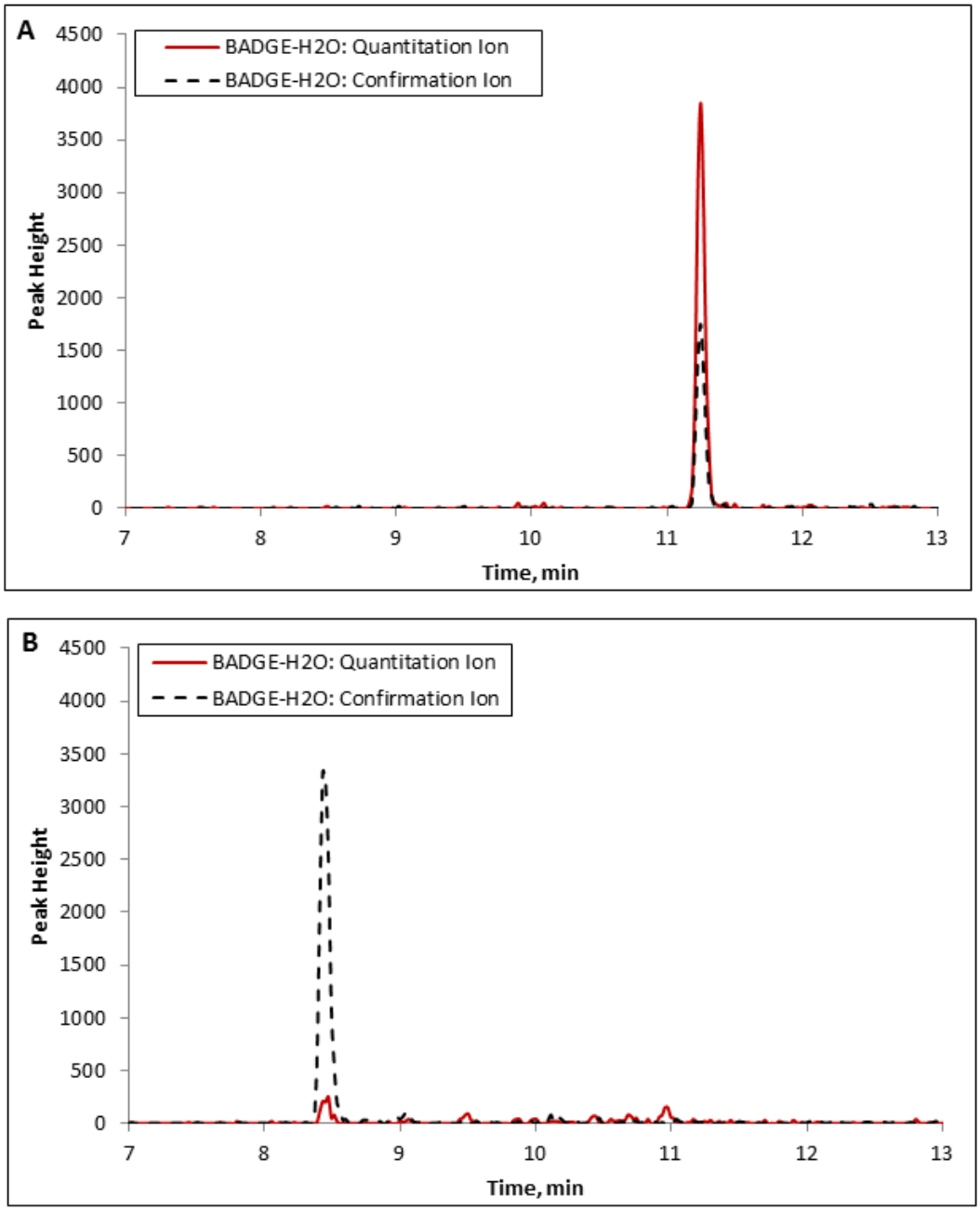


Figure 2.29 LC/MS/MS chromatograms from FD2 illustrating the unknown compound similar to BADGE-H2O. A) Chromatogram for a 10 µg/L BADGE-H_2O standard. B) Chromatogram for sample R-Pb08-24H (reflushed LSL section 08, filled with chlorinated pH 8 extraction water and held for 24 hours) showing a compound at earlier retention time and with quantitation and confirmation ions inverted relative to those of BADGE-H_2O.

Table 2.11 Detection an unknown BADGE-H_2O-like compound (8.5 min retention time) eluting from epoxy-coated pipe sections in FD2.

Extraction Water and Holding Time	BADGE-H_2O-like compound eluting at 8.5 min			
	LSLs		CSLs	
	Response Factor	µg/L*	Response Factor	µg/L*
Chlorinated pH 8 Extraction Water (0 h)	ND	ND	ND	ND
Pipe08: 6 h	1.18	98	0.0327	26
Pipe02: 24 h	0.0363	2.7	0.0443	3.2
Pipe05: 24 h	0.0440	3.2	0.129	9.6
Pipe09: 24 h	0.125	9.3	0.0417	2.9
Chlorinated pH 8 Extraction Water (0 h)	ND	ND	ND	ND
Pipe02: 24 h, then 7d	0.0348	1.8	0.0661	4.8
Pipe05: 24 h, then 7d	0.0407	2.2	0.0882	7.7
Pipe09: 24 h, then 7d	0.145	13	0.125	11
Reflushed, then:				
Chlorinated pH 8 Extraction Water (0 h)	ND	ND	ND	ND
Pipe02: 6 h	ND	ND	ND	ND
Pipe05: 6 h	ND	ND	0.0232	0.85
Pipe08: 6 h	0.142	9.8	0.0467	3.2
Pipe09: 6 h	0.0521	3.1	0.0412	2.2
Chlorinated pH 8 Extraction Water (0 h)	ND	ND	ND	ND
Pipe02: 6 h, then 24 h	0.00590	ND	0.0101	ND
Pipe05: 6 h, then 24 h	0.00529	ND	0.0348	1.8
Pipe08: 6 h, then 24 h	0.145	11	0.0469	2.9
Pipe09: 6 h, then 24 h	0.0501	2.9	0.0579	3.5
Chlorinated pH 8 Extraction Water (0 h)	ND	ND	ND	ND
Pipe02: 6 h, then 24 h, then 7d	0.0160	1.4	0.0399	4.4
Pipe05: 6 h, then 24 h, then 7d	0.0135	1.1	0.0401	4.4
Pipe08: 6 h, then 24 h, then 7d	0.143	17	0.0651	7.5
Pipe09: 6 h, then 24 h, then 7d	0.0541	6.1	0.0692	8.0

*Assuming a response factor the same as that of BADGE-H_2O

Pipe08 was exposed to chlorinated extraction water in FD1, Pipe02 was stored wet, and Pipe09 was not used in FD1.

Table 2.12 BPA and BPA-like compounds detected in extraction waters of the second epoxy-coating fill-and-dump experiment (FD2).

Extraction Water and Holding Time	BPA, µg/L 6.6 min RT		BPA-like, µg/L* 4.5 to 5.9 min RT		BPA-like, µg/L* 6.0 to 6.4 min RT	
	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs
Chlorinated pH 8 Extraction Water (0 h)	0.22	0.22	ND	ND	ND	ND
Pipe08: 6 h	10	9.8	12	0.79	120	43
Pipe02: 24 h	9.0	1.1	0.83	0.21	27	17
Pipe05: 24 h	10	2.3	0.17	7.9	31	46
Pipe09: 24 h	0.22	0.22	0.75	13	179	194
Chlorinated pH 8 Extraction Water (0 h)	0.059	0.059	ND	ND	ND	ND
Pipe02: 24 h, then 7d	2.8	1.2	3.3	6.0	30	40
Pipe05: 24 h, then 7d	2.6	2.4	2.9	10	32	68
Pipe09: 24 h, then 7d	2.1	2.2	9.9	17	163	129
Reflushed, then:						
Chlorinated pH 8 Extraction Water (0 h)	≤ 0.057	≤ 0.057	ND	ND	ND	ND
Pipe02: 6 h	0.83	≤ 0.057	0.51	0.37	4.0	5.5
Pipe05: 6 h	0.24	0.75	0.33	3.4	5.8	15
Pipe08: 6 h	1.3	0.87	12	5.3	83	31
Pipe09: 6 h	2.2	≤ 0.057	5.9	5.1	37	23
Chlorinated pH 8 Extraction Water (0 h)	0.035	0.035	ND	ND	ND	ND
Pipe02: 6 h, then 24 h	0.42	≤ 0.057	0.53	0.44	14	13
Pipe05: 6 h, then 24 h	0.52	1.6	2.8	3.0	7.5	29
Pipe08: 6 h, then 24 h	1.8	2.1	10	4.9	79	37
Pipe09: 6 h, then 24 h	1.2	1.8	3.6	4.3	33	35
Chlorinated pH 8 Extraction Water (0 h)	0.038	0.038	ND	ND	ND	ND
Pipe02: 6 h, then 24 h, then 7d	12	10	18	2.7	74	97
Pipe05: 6 h, then 24 h, then 7d	12	9.1	13	22	69	91
Pipe08: 6 h, then 24 h, then 7d	10	11	60	37	136	97
Pipe09: 6 h, then 24 h, then 7d	8.5	10	32	35	83	106

*Assuming a response factor the same as that of BPA ND = not detected

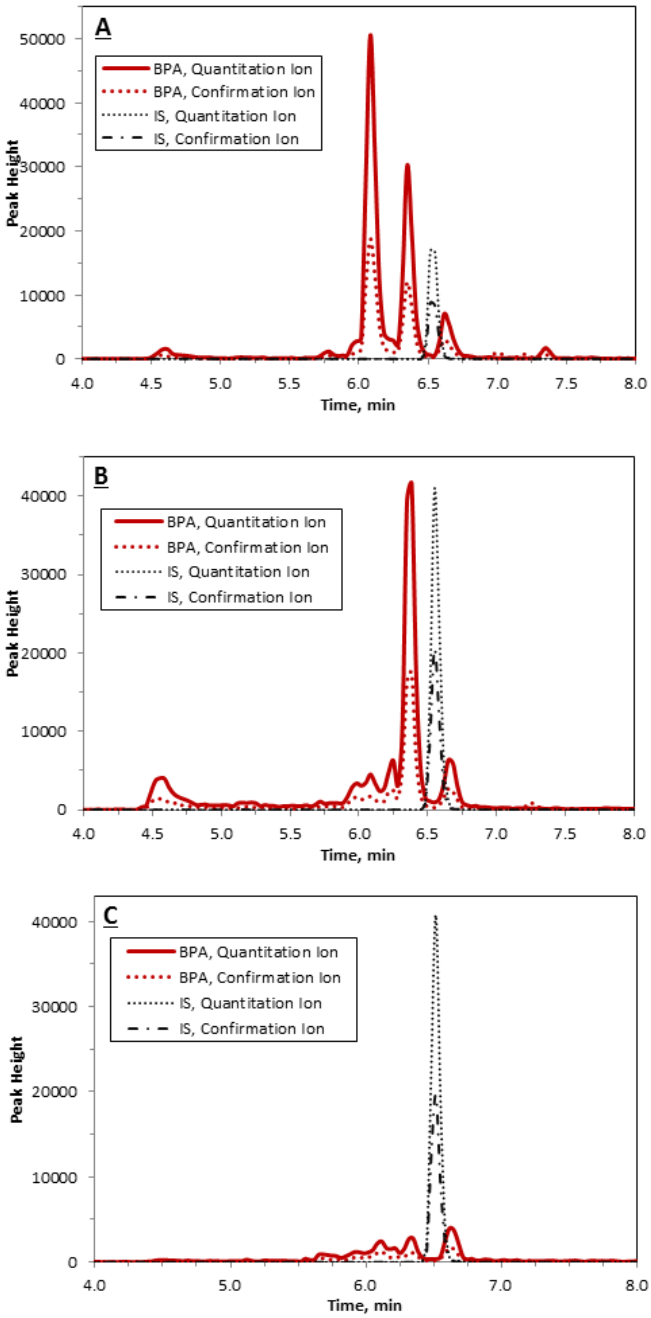


Figure 2.30 LC/MS/MS chromatograms from FD2 illustrating BPA-like compounds with retention times differing from that of BPA (BPA retention time is 6.6 min). A) Chromatogram from sample Pb08-6H (epoxy-coated LSL section filled with chlorinated pH 8 extraction water in FD1, not reflushed, filled with chlorinated pH 8 extraction water, and held for 6 hours). B) Chromatogram from sample Cu02-7D (epoxy-coated CSL section, filled with dechlorinated pH 8 tap water and pH 6.5 extraction water during FD1, not reflushed, filled with chlorinated pH 8 extraction water, then held for 7 days). C) Chromatogram from sample Pb02-R-6H (epoxy-coated LSL section, filled with dechlorinated pH 8 tap water and pH 6.5 extraction water during FD1, reflushed, filled with chlorinated pH 8 extraction water, and held for 6 hours.

Table 2.13 Residual chlorine* data for epoxy-coated pipe sections in FD2.

Extraction Water and Holding Time	Residual Cl_2, mg/L as Cl_2	
	LSLs	**CSLs**
Chlorinated pH 8 Extraction Water (control = 0 h)	1.98	1.98
Chlorinated pH 8 Extraction Water (control = 6 h)	1.97	1.97
Pipe08: 6 h	0.53	0.38
Pipe02: 24 h	0.04	0.08
Pipe05: 24 h	0.07	0.14
Pipe09: 24 h	0.18	0.19
Chlorinated pH 8 Extraction Water (control = 0 h)	1.90	1.90
Pipe02: 24 h, then 7d	0.02	0.03
Pipe05: 24 h, then 7d	0.02	0.03
Pipe09: 24 h, then 7d	0.04	0.04
Pipes reflushed and then:		
Chlorinated pH 8 Extraction Water (control = 0 h)	1.93	1.93
Pipe02: 6 h	0.13	0.20
Pipe05: 6 h	0.17	0.18
Pipe08: 6 h	0.36	0.22
Pipe09: 6 h	0.17	0.21
Chlorinated pH 8 Extraction Water (control = 0 h)	2.02	2.02
Pipe02: 6 h, then 24 h	0.03	0.06
Pipe05: 6 h, then 24 h	0.04	<0.02
Pipe08: 6 h, then 24 h	0.12	0.06
Pipe09: 6 h, then 24 h	0.06	0.07

LSLs = Lead service lines CSLs = Copper service lines

*Measured with the HACH Total Chlorine Method 8167; selected samples were spot tested to verify the absence of combined chlorine.

2.3.4.4 PET Liner Fill-and-Dump Experiment (FD3)

The FD3 PET liner experimental results are summarized in Tables 2.14 and 2.15 and show no detection of phthalate esters and phthalic acids. To investigate if leaching of these compounds from the PET liner could be induced under more extreme conditions, pieces of the liner were exposed to hexane:chloroform (50:50), acetonitrile, and methanol:water (10:90). These exposures to organic solvents still yielded no detection of the phthalate esters or phthalic acids. The lack of leaching is likely attributable to the purity of the PET used in the liners. Products made from virgin PET leach very few phthalates, but products made with recycled PET have been found to leach phthalates.[19,63,64]

During the FD3 experiment, 23 to 90% of the starting chlorine concentration was consumed (Table 2.16), most like due to impurities present in the pipe or end-fittings and not reaction with the PET itself. In comparison to the results for the epoxy coating, the rate of chlorine consumption was slower: an average of only 17% consumption after 6 hours, compared to 88% for the epoxy coating. Breault[55] explored the chlorination of this PET liner in more detail and reported that no further chlorine demand was observed when a PET-lined pipe section was refilled with chlorinated pH 8 extraction water for the third time, whereas the chlorine demand associated with epoxy-coated pipe sections persisted after repeated exposure to both high and low concentrations of chlorine.

Table 2.14 Phthalate esters detected in extraction waters of the PET liner fill-and-dump experiment (FD3).

Extraction Water and Holding Time	BBP, µg/L		DEHP, µg/L		DEP, µg/L		DETP, µg/L		DMIP, µg/L		DMP, µg/L		DMTP, µg/L	
	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs
Dechlorinated Tap Water, pH 8	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
Control (unlined) – 6 h	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h (A)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h (B)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
24 h	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
4 d	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
Chlorinated pH 8 Extraction Water	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
24 h	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
4 d	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
Low-pH Extraction Water, pH 6.5	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
Control (unlined, 6 h dechlorinated tap water)														
6 h	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h, then 4 d	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h dechlorinated tap water														
6 h (A)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h (B)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h, then 4 d (A)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h, then 4 d (B)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h chlorinated pH 8 reagent water														
6 h	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h, then 4 d	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1

Table 2.15 Phthalate esters and phthalic acids detected in extraction waters of the PET liner fill-and-dump experiment (FD3).

Extraction Water and Holding Time	DNBP, µg/L		DNOP, µg/L		DEHA, µg/L		PA, µg/L		IPA, µg/L		TPA, µg/L	
	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs
Dechlorinated Tap Water, pH 8	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 4	≤ 4	≤ 2	≤ 2	≤ 3	≤ 3
Control (unlined) – 6 h	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 4	≤ 4	≤ 2	≤ 2	≤ 3	≤ 3
6 h (A)	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 4	≤ 4	≤ 2	≤ 2	≤ 3	≤ 3
6 h (B)	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 4	≤ 4	≤ 2	≤ 2	≤ 3	≤ 3
24 h	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 4	≤ 4	≤ 2	≤ 2	≤ 3	≤ 3
4 d	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 4	≤ 4	≤ 2	≤ 2	≤ 3	≤ 3
Chlorinated pH 8 Extraction Water	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
24 h	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
4 d	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
Low-pH Extraction Water, pH 6.5	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
Control (unlined, 6 h dechlorinated tap water)												
6 h	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h, then 4 d	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h dechlorinated tap water												
6 h (A)	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h (B)	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h, then 4 d (A)	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h, then 4 d (B)	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h chlorinated pH 8 reagent water												
6 h	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h, then 4 d	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7

Table 2.16 Residual chlorine* data for PET lined pipe sections in FD3.

Extraction Water and Holding Time	Residual Cl_2, mg/L as Cl_2	
	LSLs	**CSLs**
Dechlorinated pH 8 Tap Water	≤ 0.02	≤ 0.02
Chlorinated pH 8 Extraction Water (control = 0 h)	1.97	1.97
Chlorinated pH 8 Extraction Water (control = 6 h)	1.98	1.98
Chlorinated pH 8 Extraction Water (control = 24 h)	1.97	1.97
Chlorinated pH 8 Extraction Water (control = 4 d)	1.95	1.95
6 h	1.54	1.72
24 h	0.99	1.45
4 d	0.82	1.15

LSLs = Lead service lines CSLs = Copper service lines

*Measured with the HACH Total Chlorine Method 8167; selected samples were spot tested to verify the absence of combined chlorine.

2.4 Conclusions

Analytical methods were developed to identify and quantify organic compounds that would potentially leach from an epoxy coating or PET liner into drinking water. Key epoxy leachates (bisphenols, BDGEs, and selected hydrolysis and chlorination by-products of these compounds) were analyzed by LC/MS/MS. Key PET leachates (PAEs and phthalic acids) were analyzed by GC/MS and LC/MS/MS, respectively. Analytical inferences were eliminated or minimized and method detection limits were low enough to provide leachate data relevant to regulatory or recommended levels.

The use of linings and coatings on small-diameter pipes (water service lines), which have relatively high ratios of surface area-to-volume and flow intermittently, maximizes the potential for high concentration of organic chemicals to leach into drinking water. Fill-and-dump sampling experiments are well suited for simulating such situations, representing reasonable well a worst-case scenario for human exposure to high concentrations of leachates in drinking water, albeit for relatively short periods of exposure.

A freshly applied potable water grade epoxy coating leached low levels of BADGE, BPA, and BPA-like compounds into water and, after aging during storage, it leached low levels of BPA and BPA-like compounds. During longer holding times, BADGE was observed hydrolyzing to BADGE-H_2O and BADGE-$2H_2O$. Exposing the epoxy coating to chlorinated water slightly increased leached organics. Leached BPA and BADGE levels were well below NSF's recommended drinking water total allowable concentrations (100 µg/L for BPA and 1000 µg/L for BADGE).[35] Phthalate esters and phthalic acids were not detected in water samples collected, in a fill-and-dump experiment, from pipe sections lined with a potable water grade PET liner.

Preliminary chlorination experiments demonstrated that all bisphenols studied (i.e., BPA, BPB, BPD, BPE, and BPS) were susceptible to chlorination and chloramination. Bisphenol reactions with free chlorine were very rapid and future experiments should employ sampling on minute timescales. Bisphenol reactions with monochloramine were slower reactions and should be sampled with hour timescales. BADGE was found unreactive with both free and combined chlorine (monochloramine).

2.5 References

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Chapter 3: Epoxy Leachates with Similarity to Bisphenol A and Implications for Analysis

3.1 Introduction

Bisphenol A (BPA) has been extensively used in epoxy coatings due to the versatility of its polymeric products. BPA is also used as an additive, in monomeric form, in a wide variety of products, including bottles, food packaging, medical/healthcare supplies, dental sealants, membranes (e.g., in hemodialysis, beverage concentration, and ultra-pure water applications), appliances, construction materials, coatings (food and marine applications), electrical and electronic components, optical media, automotive parts and materials, plumbing materials, adhesives, and photocured composites.[1] BPA can also be found as a chemical additive in thermal paper (receipts), polyvinyl chloride, hydraulic brake fluids, and tires.[1] While some manufacturers have switched or considered switching from BPA to other similar compounds, such as bisphenol B, F, E, or S (BPB, BPF, BPE, or BPS, respectively), BPA is still widely used.[2-4]

The frequent and widespread use of BPA has led to detectable levels in food, water, dust, and air, with the main exposure risk to humans through consumption of food and water.[5,6] Epoxy coatings on food packaging and containers can leach BPA into a wide variety of food products.[7,8] When a BPA-based epoxy coating is used on food cans and is in contact with both liquid and solid food phases, BPA tends to partition into the solid phase[9] which can increase consumption risk. Leaching is affected by storage temperature[6], type of material in contact with the epoxy[10], time (product expiration date)[10], specific product lots and manufacturer[9], and contact with equipment that processes the food prior to canning[11].

The two main sources of BPA in water are contamination of the source supply[12-14] and leaching from materials in contact with the drinking water[15,16]. Epoxy coatings can be used on

the interior (and exterior) surfaces of drinking water service lines, pipes (mains), and storage tanks. There are two main active compounds in epoxy starting materials: a prepolymer such as bisphenol A diglycidyl ether (BADGE) and a hardener such as triethylenetetramine (TETA). BADGE is produced by reacting BPA with an epichlorohydrin to yield a compound with reactive side chains. TETA is a polyamine that facilitates polymerization of BADGE. Epoxy coatings can potentially leach starting materials (such as BPA, BADGE, or TETA) or partially polymerized products into food or water. The leaching potential is expected to decrease as the epoxy cures, but for drinking water applications there is also concern about the release or formation of organic compounds as disinfectants react with epoxy coatings or with compounds leaching from epoxy coatings.[17,18]

Concerns have been raised about the safety of chronic low-level exposure to BPA, since it is a known endocrine disruptor (i.e., a xenoestrogen). In response to these concerns, various studies have examined correlations between elevated levels of BPA and negative impacts on reproduction, neurobehavioral development, and metabolic diseases (e.g., obesity, diabetes, heart and kidney dieseases, thyroid and liver function)[19,20]; but these and other studies have not demonstrated a causal relationship between environmentally relevant concentrations of BPA and adverse impacts on human health. To date, neither the U.S. Environmental Protection Agency[21] (EPA) nor U.S. Food and Drug Administration[22] has chosen to regulate BPA; and BPA did not meet EPA's screening criteria for inclusion on the third candidate contaminant list (CCL3)[21] for future drinking water regulations, nor is it included in the draft of the fourth list (CCL4). The EPA[21] and European Food Safety Authority[23] recommend a BPA oral reference dose or intake limit of 0.05 mg/kg-bw/day (mg per kg of body weight per day). For BPA in drinking

water, the National Sanitation Foundation (NSF) recommends a single-product allowable concentration of 0.01 mg/L and a total allowable concentration of 0.1 mg/L.[24]

Although much attention has focused on BPA and BADGE, there are other compounds that can leach from epoxy coatings. Industrial grade BPA has been reported to contain several impurities that are degradates, by-products, or polymerized by-products of BPA.[25] The starting materials are extensively cross-liked during the curing process; however, a small percentage of the starting materials will remain unreacted, and these and various intermediates (by-products) of the polymerization process can potentially leach out of the coating.[26] Can coatings that contain BPF are created from a novolac glycidyl ether (NOGE) mixture that contains 30 to 40% 2-ring NOGE (also known as bisphenol F diglycidyl ether, BFDGE), while the remaining percentage is a mixture of BFDGE isomers and 3 to 8-ring NOGE compounds.[27] The 2- to 6-ringed NOGE compounds have been reported leaching into food products.[28,29] Similarly, there is potential for drinking water epoxy coatings to leach unreacted starting materials, impurities, or partially polymerized by-products.

An additional concern with epoxy leachates is the interactions with the surrounding environment. Canned foods contain amino acids, proteins, and sugars that can react with leachates, and BADGE does have reactivity with amino acids and sugars.[30] Epoxy leachates in drinking water are exposed to disinfectants, most commonly free chorine (Cl_2/HOCl/OCl^-) or monochloramine (MCA or NH_2Cl) and there are known chlorinated by-products of BPA[31] and BADGE[32]. Such reactions lead to concern about changes in toxicity, i.e., whether the byproducts are more or less toxic than the parent compounds. In drinking water, BADGE and BFDGE are also susceptible to hydrolysis and their hydrolysis by-products (e.g., BADGE-H_2O, BADGE-$2H_2O$,

BADGE-H_2O-HCl, BFDGE-H_2O, BFDGE-$2H_2O$, and BFDGE-H_2O-HCl) have been observed in food products.[29,30,33-37]

A recent publication by Lane *et al.*[18] explored the leaching of organics from a two-part potable-water-grade BADGE (BPA) based epoxy. Key leachates were determined to be BADGE and a compound that analytically mimicked BPA in that it was detected by LC/MS/MS using the same quantitation and confirmation ions as BPA. Other compounds of this nature, herein referred to as "BPA-like" compounds, were detected in the experiments summarized by Lane *et al.*[18] and in subsequent experiments described below. All but one of these BPA-like compounds had shorter LC retention times than the 6.6 min retention time observed for *para*,*para'*-BPA (*p,p'*-BPA), the isomer preferentially used in commercial applications. A major BPA-like peak was often observed at 6.0 min, corresponding to what is herein referred to as BPA-like compound A; and another BPA-like peak, often smaller than the peak at 6.0 min, was often observed eluting at 6.3 min (BPA-like compound B). Other, minor BPA-like peaks were often observed at shorter retention times. While the detection of BPA-like compound A was noted by Lane *et al.*[18], efforts to identify this and other BPA-like compounds, and to elucidate their chemical structures, were not previously reported.

Due to concerns regarding BPA and BADGE in foods and drinking water, it is important to know whether one or more BPA-like compounds may be "hiding" from traditional LC/MS/MS analysis. Ackerman *et. al.*[37] reported two BPA-like compounds leaching from an epoxy liner of infant formulas and identified them through LC/MS/MS and NMR as BADGE-$2H_2O$ and the bisphenol A monoglycidyl ether hydrolysis by-product BAMGE-H_2O[38]. BADGE-$2H_2O$ and BAMGE-H_2O were found to mimic BPA during negative mode electrospray LC/MS/MS experiments.[38]

The purpose of this paper is to document the presence of BPA-like compounds in water exposed to a potable water grade epoxy coating, to summarize efforts to identify them, and to present evidence that the BPA-like compounds could be adducts or BADGE hydrolysis products. BPA-like compound A often produced the largest BPA-like peak in epoxy leachate chromatograms and was, therefore, the primary focus of study.

3.2 Materials and Methods

3.2.1 Reagents and Chemicals

A mixture of potable-water-grade epoxy resin (part A) and hardener (part B) was prepared and then applied by the manufacturer to form an epoxy coating on the interior surfaces of a series of lead and copper pipe sections.[39] Reagent water was prepared using a Millipore Elix Reverse Osmosis system followed by a Millipore A10 unit. Tap water was collected after allowing the water tap to run for at least 5 min prior to collection. Solid phase extraction cartridges (Sep-Pak Vac 6cc, tC18) were purchased from Waters Corporation (Milford, MA). Hydrochloric acid, glacial acetic acid, laboratory grade sodium hypochlorite solution, LC/MS grade methanol (Optima), sodium hydroxide solution, calcium chloride dehydrate, monobasic and dibasic sodium phosphate, sodium bicarbonate, sodium bisulfite, sodium chloride, cupric sulfate pentahydrate, ferrous ammonium sulfate hexahydrate, lead (II) chloride, and magnesium chloride hexahydrate were purchased from Fisher Scientific (Pittsburgh, PA). Ammonium formate, formic acid, and triethylenetetramine (TETA) were purchased from Sigma Aldrich (St. Louis, MO). The *p,p'*-bisphenols (BPA, BPB, BPD, and BPE) were purchased from TCI America (Portland, OR); 2,2-bis(4-hydroxy-3-methylphenyl)propane (*p,p'*-BPA-2CH3), 3,4'-isopropylidenediphenol (*m,p'*-BPA), 1-methoxy-4-(4-methoxybenzyl)benzene (*p,p'*-BPF-2CH3),

BADGE (*p,p'*-BADGE) and bisphenol F (*p,p'*-BPF) from Sigma Aldrich (St. Louis, MO); and 2,2'-Bis(hydroxyphenyl)methane (*o,o'*-BPF) from Toronto Chemical Company Inc. (Toronto, Ontario, Canada). Deuterated internal standards, BPA-D8 and sulfamethoxazole-D4 (SMXL-D4), were ordered from Cambridge Isotopes Laboratory (Tewksbury, MA) and Toronto Research Company (Toronto, Ontario, Canada), respectively.

3.2.2 Analytical Methods

3.2.2.1 LC/MS

The LC system consisted of a Shimadzu (Columbia, MD) Prominence High Performance LC (HPLC) equipped with a LC-20AB binary pump, DGU-20A3 degasser, and SIL-20A autosampler. Chromatographic separation was obtained with a reverse phase Gemini-NX C18-with-TMS-endcapping column, 150 × 3.0 mm, 3-micron particle size (Phenomenex, Torrance, CA), at a flow rate of 0.4 mL/min. A 4000 QTrap triple-quadrupole linear ion-trap mass spectrometer with a turbo ion-spray source (AB SciEx, Framingham, MA) was used for detection and operated in scan and multiple reaction monitoring (MRM) modes with nitrogen gas for nebulization of the electrospray source. Specific MS and LC parameters can be found in a prior publication.[18] BPA-D8 was selected as the internal standard for the bisphenols, and SMXL-D4 as the bisphenol diglycidyl ether internal standard. The method detection limits (MDL) were determined per *Standard Methods* (Method 1030C, Method Detection Limit)[40] and were 0.057 µg/L for BPA[18] and 7.0 µg/L for BADGE[18]. BPA-like compounds were quantitated assuming a response equivalent to BPA, but concentrations below the equivalent MDL for BPA were reported as non-detectable (ND) since calculated MDLs were unavailable. The quantitation-to-

confirmation-ion ratio was calculated for BPA calibration standards and the BPA-like compounds were considered matching if their ratios were within ± 20% of BPA.

3.2.2.2 GC/MS

Solid phase extraction was used to prepare samples for analysis of bisphenols using gas chromatography/mass spectrometry (GC/MS). The procedure was based on a technical note from United Chem[41]; the sample was drawn through solid phase extraction cartridge under vacuum at 5 mL per min; the internal standard was not added, nor was the sample derivatized. An Agilent (Agilent Technologies, Santa Clara, CA) 6890A GC with 5973N MS and 7683 autosampler was operated in scan mode from 40 to 550 amu. The carrier gas was helium held at a flow rate of 1-mL/min. A 1.0-µm aliquot of sample was injected while the inlet and transfer line were held at 270˚C. Separation was achieved with an HP-5MS 0.25-mm ID × 30 m column with a 0.25-µm film thickness. After a 3.5-min solvent delay, the oven temperature was held at 100°C for 1 min and then ramped at 9°C/min to 300°C. Samples were also analyzed on a Quattro Micro GC Agilent 6890N GC in the University of Kansas Mass Spectrometry & Analytical Proteomics Laboratory. Run conditions and parameters on this GC/MS were similar to those described above.

3.2.2.3 TOF

Time-of-Flight (TOF) mass spectrometry analysis was performed by the University of Kansas (KU) Mass Spectrometry & Analytical Proteomics Laboratory on a Micromass Q-TOF-2 mass spectrometer (Micromass Ltd., Manchester UK).

3.2.3 Fill-and-Dump Pipe Sampling

Two fill-and-dump (FD) experiments were conducted in which 4-ft. long sections of 1.59 cm (inner diameter) lead and copper service lines were filled with water to study leaching of organic compounds from epoxy coatings. The purpose of the first set of fill-and-dump experiments (FD1) was to examine organic compounds leached from freshly applied epoxy coatings. The purpose of the second fill-and-dump experiment (FD2) was to examine leaching after the pipe sections were stored for a period of time under wet versus dry conditions.

For the initial fill-and-dump investigation (FD1), a potable water grade epoxy coating was applied by the manufacturer to the inside of each of lead or copper service line, except for the controls, which were unlined lead and copper pipe sections. The epoxy was cured for 48 hours and the pipe sections were then flushed for 15 min with cold tap water to remove any particles or readily dissolved materials.[42] The extraction waters used to fill the pipe sections were similar to those specified by the National Sanitation Foundation (NSF)[24], but our extraction procedure differed from that specified by NSF, such that our results could differ from those reported by NSF.

Three extraction waters were used: dechlorinated pH 8 tap water (DT), chlorinated pH 8 extraction water (CL), and pH 6.5 extraction water (LP, with the lower pH intended to more aggressively solubilize metals, especially lead and copper). The dechlorinated tap water was prepared by dechlorinating with sodium bisulfite (chlorine removal was confirmed with HACH Total Chlorine Method 8167[43]) and then adjusting the pH of tap water to 8.0 ± 0.1 using 1.0 and 0.1 N HCl (and 0.1 N NaOH). Chlorinated pH 8 extraction water was 1 mM sodium bicarbonate, with 1 mM $CaCl_2$ added as a source of water hardness, sodium hypochlorite solution added to

produce a free chlorine residual of 2 mg/L as Cl_2, and the pH adjusted to 8.0 ± 0.1 using HCl and NaOH. The pH 6.5 extraction water was 1 mM sodium carbonate, with 1 mM $CaCl_2$ added as a source of water hardness and the pH adjusted to 6.5 ± 0.1 with HCl and NaOH. The extraction waters were held in the pipe sections at room temperature (controlled at 20–25 °C) for 0.25, 1, 4, 7, and 10 days and then analyzed for bisphenols (BPA, BPB, BPD, BPE, and BPF) and BADGE.[42,44]

The second fill-and-dump experiment (FD2) was conducted with selected epoxy-coated pipes used in FD1, the uncoated (control) pipe sections from FD1, and two epoxy-coated pipes that had been stored dry (for additional curing time) and were not filled during FD1. All of the pipes had been stored at room temperature for seven months. Some were stored wet (filled with reagent water) and some dry. After being removed from storage (and emptied if needed), the pipe sections were rinsed with 100 mL of reagent water and then filled with chlorinated pH 8 extraction water. The extraction water was prepared as before, but with 0.56 mM sodium bicarbonate (instead of 1 mM sodium bicarbonate) and 0.44 mM NaCl, so that the initial pH would be about 8.0 and would require little or no adjustment. The extraction water was held in the pipe sections at room temperature (20–25 °C) for 6 to 24 h. After samples were collected for analysis of bisphenols and BADGE, the pipe sections were refilled with chlorinated pH 8 extraction water and held for 7 more days before a second set of samples was collected. All pipe sections were then flushed for 15 min with cold tap water, rinsed with 100 mL of reagent water, and then refilled with chlorinated pH 8 extraction water. Six hours later, samples were collected for analysis of bisphenols and BADGE. The pipe sections were then refilled, held for 1

d and sampled again; they were then refilled one last time, then held for 7 d. In every case, the pipe sections were stored at room temperature (20–25 °C).

3.2.4 BPA Adduct Formation

To investigate adduct formation, a series of vials were filled with various solutions, each containing a potential adduct-forming compound of interest. The compounds examined were lead ($PbCl_2$) and copper (CuSO4), salts of various ions typically found in drinking water (i.e., ammonium bicarbonate, calcium chloride, magnesium chloride, and ferrous ammonium sulfate) and the common epoxy hardener TETA (part B). Concentrations of the potential complexing agents were in significant excess relative to the BPA concentration of 80 µg/L (0.00035 mM), and samples were collected at contact times of 0, 1, 11, 13, 18, 32, and 201 days (Appendix Table A.2.1.1).

3.3 Results and Discussion

3.3.1 Detection of BPA-like Compounds

In the extraction water samples from the first fill-and-dump experiment (FD1), BPA and BADGE concentrations ranged from ≤ 0.057 to 2.0 µg/L and from ≤ 7.0 to 277 µg/L, respectively (Table 3.1 and Appendix Table A.2.1.2). Additional peaks were observed (Figure 3.1) with shorter retention times than BPA: a major peak at 6.0 min (BPA-like compound A) and a minor peak at 6.3 min (BPA-like compound B). BPA elutes at 6.6 min. BPA-like compounds A and B had MS MRM transitions identical to those of BPA (quantitation transition: 227.0 → 212.0 and confirmation transition: 227.0 → 133.0) and the same quantitation-to-confirmation-ion ratio. This result was reproduced by KU's Mass Spectrometry & Analytical Proteomics Laboratory when they observed BPA-like compound A eluting 0.5 min earlier than BPA on their reverse

phase C18 LC column. BPA-like compound A was present in 28 of the 30 pipe samples and BPA-like compound B in 21 of the 30 pipe samples; the highest levels were detected in pipe sections filled with chlorinated pH 8 extraction water. Because of identical MRM transitions, BPA-like compounds A and B were thought to have structural similarity to BPA, so a BPA calibration curve was used to estimate their concentrations. On this basis, BPA-like compound A concentrations ranged from non-detectable to 94 µg/L and the BPA-like compound B from non-detectable to 51 µg/L.

To test the possibility that matrix effects in solution were causing BPA's retention time to shift, a BPA standard was spiked into selected samples. The resulting chromatograms showed a distinct peak for BPA, at its normal retention time, as well as the additional compounds at shorter retention times but with identical quantification-to-confirmation-ion ratios (Figure 3.2). A BPA matrix spike was prepared using each of the three extraction waters and the BPA retention time remained at 6.6 min. Because BPA did not shift retention time, the BPA-like compounds eluting at an earlier time were clearly distinctly different compounds from BPA, despite their apparent structural similarity.

The first set of results from the second fill-and-dump experiment (FD2) showed that, after extended storage but before being reflushed, the epoxy coatings leached both BPA and BPA-like compounds, but not BADGE (Table 3.2 and Appendix Table A.2.1.3). The pipes that were stored dry, and not extracted in FD1, yielded the highest concentrations of BPA and BPA-like compounds. BPA concentrations ranged from 1.1 to 10 µg/L, BPA-like compound A from 4.4 to 161 µg/L, and BPA-like compound B from 12 to 71 µg/L (Table 2; top portion of table, for tests before flushing the stored pipe sections).

After the stored pipe sections were flushed with tap water and rinsed with reagent water, leachates were still observed (Table 3.2). BADGE was not detected, BPA concentrations ranged from non-detectable to 12 µg/L, BPA-like compound A from non-detectable to 48 µg/L, and BPA-like compound B from 1.7 to 136 µg/L (Table 3.2; bottom portion of table, after flushing). Pipes exposed to free chlorine during the first fill-and-dump experiment (FD1) leached slightly higher levels of BPA and BPA-like compounds.

In addition to the BPA-like compounds A and B, additional minor BPA-like peaks were observed with approximate elution times of 4.4, 5.7, 5.9, and 7.4 min. The shapes of these minor peaks were not as well defined as those of BPA-like compounds A and B (Appendix Figure A.2.2.1) and the quantitation-to-confirmation-ion ratios of these peaks did not always match those of BPA (Appendix Table A.2.1.4). The BPA-like compound with an elution time of 4.4 min was detected in 34 of the 38 samples (but matched the BPA quantitation-to-confirmation-ion ratio in only 19 samples); the BPA-like compound with an elution time of 5.7 min was detected in 26 of the 38 samples (but matched the BPA quantitation-to-confirmation-ion ratio in only 17 samples); the BPA-like compound with an elution time of 5.9 min was detected in 11 of the 38 samples (and matched the BPA quantitation-to-confirmation-ion ratio in 10 samples); and the BPA-like compound with an elution time of 7.4 min was detected in 14 of the 38 samples (but matched the BPA quantitation-to-confirmation-ion ratio in only 4 cases). For the minor BPA-like peaks that matched the BPA quantitation-to-confirmation-ion ratio, concentrations ranged from non-detectable to 58 µg/L (Appendix Table A.2.1.4).

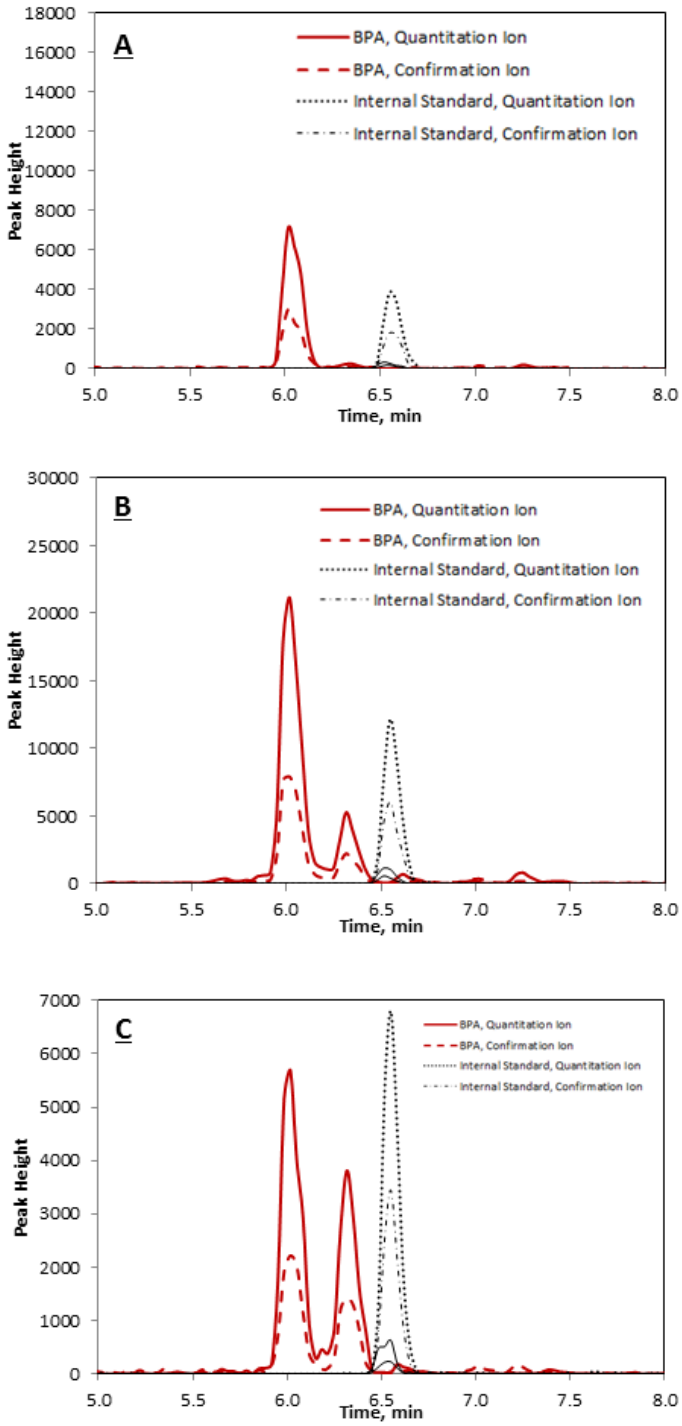


Figure 3.1 LC/MS/MS chromatograms from FD1 illustrating BPA-like compounds with retention times differing from that of BPA (BPA retention time is the same as the internal standard). A) Chromatogram from sample DT-Pb-6A (epoxy-coated lead pipe filled with dechlorinated pH 8 tap water and held for 6 hours). B) Chromatogram from sample CL-Pb-6 (epoxy-coated lead pipe filled with chlorinated pH 8 extraction water and held for 6 hours). C) Chromatogram from sample LP-Cu-6 (epoxy-coated copper pipe filled with low pH extraction water and held for 6 hours).

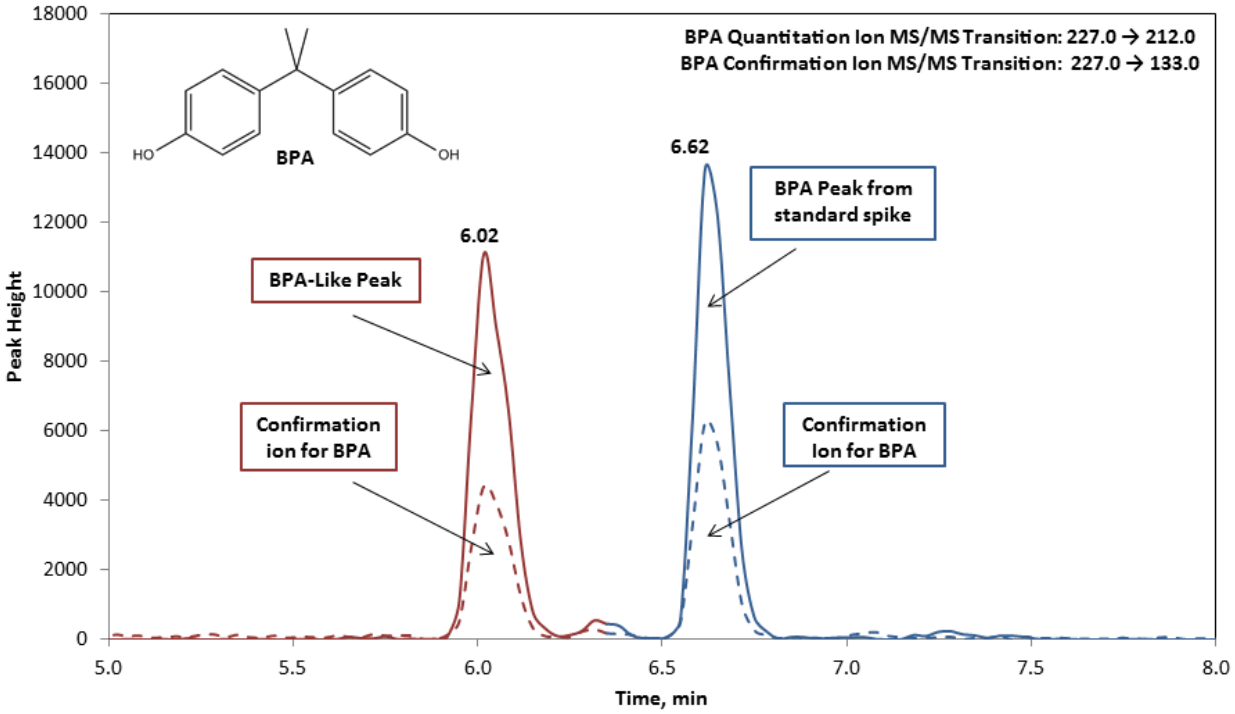


Figure 3.2 LC/MS/MS chromatogram from FD1 sample DT-Pb-6H (epoxy-coated lead pipe filled with dechlorinated pH 8 tap water and held for 6 hours) with a 40 µg/L BPA standard spiked into the sample.

Table 3.1 Maximum and minimum analyte concentrations from fill-and-dump experiment 1 (FD1) investigating leaching from pipe sections freshly coated with epoxy (additional data available in supporting information Appendix Table A.2.1.1).

	BPA-Like Compound A, µg/L				BPA-Like Compound B, µg/L				BPA, µg/L				BADGE, µg/L			
Extraction Water	**Min.**	**HT**	**Max.**	**HT**	**Min.**	**HT**	**Max.**	**HT**	**Min.**	**HT**	**Max.**	**HT**	**Min.**	**HT**	**Max.**	**HT**
Control, dechlorinated pH 8 tap water	ND	6 h	0.94	6 h	ND	All	ND	All	0.33	6 h	0.37	6 h	≤ 7.0	All	≤ 7.0	All
Control, pH 6.5 extraction water	ND	All	ND	All	ND	All	ND	All	≤ 0.057	All	≤ 0.057	All	≤ 7.0	All	≤ 7.0	All
Dechlorinated pH 8 tap water	10	10 d	68	4 d	ND	6 h	11	10 d	≤ 0.057	All	≤ 0.057	All	≤ 7.0	1 d	277	6 h
Chlorinated pH 8 extraction water	ND	10 d	94	4 d	ND	6 h	51	10 d	≤ 0.057	6 h	2.0	10 d	≤ 7.0	1 d	236	6 h
pH 6.5 extraction water*	7.4	6 h	16	4 d	ND	6 h	11	7 d	≤ 0.057	6 h	0.82	6 h	≤ 7.0	All	≤ 7.0	All
pH 6.5 extraction water**	ND	7 d	11	7 d	4.0	6 h	13	7 d	≤ 0.057	6 h	1.2	6 h	≤ 7.0	6 h	13	6 h

* pipes previously filled with dechlorinated pH 8 tap water
** pipes previously filled with chlorinated pH 8 extraction water
ND = Not detected
HT = Holding time

Table 3.2 Maximum and minimum analyte data from fill-and-dump experiment 2 (FD2) investigating leaching from stored epoxy-coated pipe sections. [Additional data available in Appendix Table A.2.1.2. Extraction waters are described in the materials and methods section and are dechlorinated pH 8 tap water (DT), chlorinated pH 8 extraction water (CL), and pH 6.5 extraction water (LP).]

Storage	FD1	BPA-Like Compound A, µg/L				BPA-like Compound B, µg/L				BPA, µg/L				BADGE, µg/L	
Condition	Extraction Water	Min.	HT	Max.	HT	Min.	HT	Max.	HT	Min.	HT	Max.	HT	Max.	HT
Before flushing for 15 min															
Dry	None*	58	7 d	161	24 h	29	6 h	71	7 d	2.1	7 d	10	24 h	≤ 7.0	all HT
Wet	DT, then LP	4.4	7 d	13	24 h	12	6 h	31	7 d	1.2	7 d	10	24 h	≤ 7.0	all HT
Dry	DT, then LP	5.6	7 d	19	24 h	14	6 h	53	7 d	1.1	24 h	8.9	24 h	≤ 7.0	all HT
Dry	CL	25	6 h	81	6 h	18	6 h	39	6 h	8.8	6 h	10	6 h	≤ 7.0	all HT
Chlorinated pH 8 Extraction Water		ND	All	ND	All	ND	All	ND	All	0.059	7 d	0.22	6 h	≤ 7.0	all HT
After flushing for 15 min															
Dry	None*	ND	7 d	20	6 h	12	6 h	106	7 d	≤ 0.057	6 h	10	7 d	≤ 7.0	all HT
Wet	DT, then LP	2.2	6 h	30	7 d	1.8	6 h	76	7 d	≤ 0.057	6 h	12	7 d	≤ 7.0	all HT
Dry	DT, then LP	ND	7 d	32	7 d	1.7	6 h	91	7 d	0.24	6 h	12	7 d	≤ 7.0	all HT
Dry	CL	ND	7 d	48	6 h	13	6 h	136	7 d	0.87	6 h	11	7 d	≤ 7.0	all HT
Chlorinated pH 8 Extraction Water		ND	All	ND	All	ND	All	ND	All	≤ 0.057	All	≤ 0.057	All	≤ 7.0	all HT

*pipe section not used in FD1 ND = Not detected HT = Holding time

Ackerman *et al*[37] observed two earlier-eluting BPA-like compounds leaching from a can lining for infant formulas. These BPA-like compounds were identified through NMR and mass spectral data as BADGE-$2H_2O$ and BAMGE-H_2O (2-(4-(2,3-dihydroxypropoxy)phenyl)-2-(4'-hydroxyphenyl) propane)); and fragmentation of BADGE-$2H_2O$ and BAMGE-H_2O in negative mode electrospray generated ions that mimicked BPA MS/MS ions.[38] This could explain some of the BPA-like peaks observed during the fill-and-dump sampling; however, in some samples, there were more than two peaks observed (Appendix Table A.2.1.4). BADGE-$2H_2O$ and BPA-like compound A were detected during FD2 and concentrations are summarized in Appendix Table A.2.1.5. For this work, BPA-like compound A was quantitated assuming a response equivalent to BPA. While this would be a reasonable assumption for a BPA adduct, the response of BADGE-$2H_2O$ could very well be different. Thus, the reported concentration should be viewed with this in mind. BPA-like compound A is similar to the peak Ackerman *et al*[38] attributed to being from the electrospray fragmentation of BADGE-$2H_2O$. BADGE-$2H_2O$ was detected in positive mode electrospray such that the negative mode instability would not have affected the reported concentrations. If BPA-like compound A was from the electrospray fragmentation of BADGE-$2H_2O$, both compounds should be detected and there should be some correlation between the two observed concentrations. Of the 38 samples from FD2: 5 samples had BADGE-$2H_2O$ with no observed BPA-like compound A, 15 samples had BPA-like compound A with no observed BADGE-$2H_2O$; and, in the 18 samples with both BADGE-$2H_2O$ and BPA-like compound A, there was no correlation between the two concentrations.

3.3.2 Retention Time Investigation

To investigate shifts in LC C18 reverse phase retention times, compounds with structures and masses similar to those of BPA were investigated. To mimic BPA during MRM mass spectrometry, a BPA-like compound must exhibit the same initial mass-to-charge (m/z 227) and same fragments (m/z 212 for quantitation, m/z 133 for confirmation) to be detected as BPA. To have the same m/z effectively requires that the BPA-like compound have the same molecular weight as BPA.

3.3.2.1 Isomers of BPA

The most commonly manufactured and sold forms of BPA and BPF are the para, para isomers *p,p'*-BPA and *p,p'*-BPF. Although less common, other isomers of the bisphenols exist. The hydroxyl group of the phenol ring is electron donating so it strongly activates the ortho (*o*) and para (*p*) positions and deactivates the meta (*m*) position of the phenol ring, thereby favoring ortho and para substitutions and making the formation of meta substituted bisphenol isomers unlikely. Experiments were performed to determine if the major and minor BPA-like peaks could be attributed to rearrangement of the hydroxyl group on the aromatic rings to give *o,p'*-BPA or *o,o'*-BPA isomers. Unfortunately, the *o,p'*-BPA and *o,o'*-BPA isomers were not commercially available. However, standards of the *m,p'*-BPA isomer (highly unlikely to be present) and an analogous compound, *o,o'*-BPF, were commercially available. BPF is structurally similar to BPA, but lacks the two methyl groups on the alkane bridge between phenolic moieties (Table 3.3).

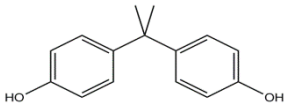
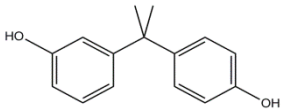
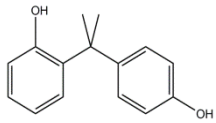
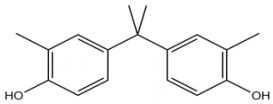
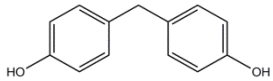
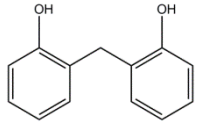
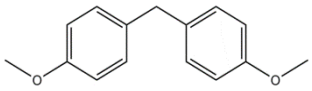
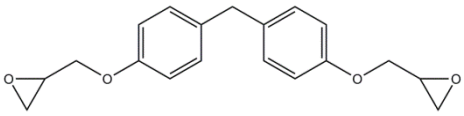
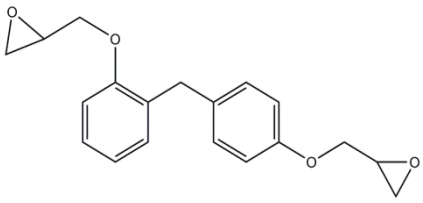
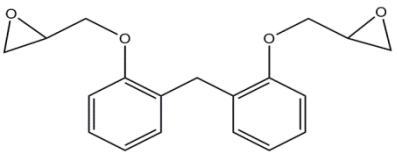
The *m,p'*-BPA and *o,o'*-BPF isomers were analyzed by LC/MS/MS. Shifting the hydroxyl group from the para to meta position in BPA resulted in a slightly longer retention time (Table

3.3). Also, moving the hydroxyl group from the para to the ortho positions in BPF (analogous to moving from *p,p'*-BPA to *o,o'*-BPA) resulted in a longer, not shorter, retention time. These results are consistent with a technical summary from Phenomenex who, using a similar reverse-phase LC column, reported that *p,p'*-BPA had an earlier elution time than *o,p'*-BPA.[45] In a related study with bisphenol F diglycidyl ether (BFDGE), *p,p'*-BFDGE eluted earlier than *o,p'*-BFDGE and *o,o'*-BFDGE.[46] Thus, both experimental and previously published results indicate that ortho ring substitution causes later elution times, not earlier times, as was the case for all of the BPA-like compounds observed except one occasionally observed at 7.4 min, whose peak was usually small and irregularly shaped, and often had a confirmation-to-quantitation-ion ratio that failed to match that of BPA. On this basis, we concluded that none of the observed BPA-like compounds were *o,p'*-BPA, *m,p'*-BPA, or *o,o'*-BPA.

3.3.2.2 Methylated Bisphenols

Another possibility considered was that one of the BPA-like compounds could have been formed by methylating the hydroxyl groups or phenol rings (ortho position) of BPF. This would also require BPF or methylated BPF to be present as an impurity in one of the starting materials. Adding two methyl groups to BPF would yield a compound having the same molecular weight as BPA and a similar MS fragmentation pattern. LC/MS/MS analysis of the methylated form of BPF (*p,p'*-BPF-2CH_3) showed that it had the same retention time as BPA (Table 3). BPF with ortho methylated phenol rings was not commercially available but BPA with ortho methylated phenol rings (*p,p'*-BPA-2CH_3) was available and had a retention time essentially the same as BPA. Since methylation of the hydroxyl groups and phenol rings did not yield the earlier retention times in the range of those observed for the BPA-like compounds,

Table 3.3 Chemical structures and experimentally determined and reported chromatographic retention times of bisphenol A and structurally similar bisphenol and bisphenol F diglycidyl ether compounds.

Abbreviation	Chemical Structure	Experimental Reverse Phase LC Retention Time, min	Reported Reverse Phase LC Retention Time, min
p,p'-BPA		6.44 4.04‡	11.50*
BPA-like	unknown	6.02 3.44‡	
m,p'-BPA		6.51	
o,p'-BPA			17.00*
p,p'-BPA-2CH_3		6.53	
p,p'-BPF		5.55	
o,o'-BPF		6.49	
p,p'-BPF-2CH_3		6.44	
p,p'-BFDGE			3.75§
o,p'-BFDGE			3.88§
o,o'-BFDGE			3.95§

*Reference 39, Phenomenex Inc. §Reference 40, Gallart-Ayala *et al.*
‡Retention time observed by KU's Mass Spectrometry & Analytical Proteomics Laboratory during LC/TOF/MS analysis

these results suggest that none of the observed BPA-like compounds were methylated forms of BPF or BPA.

3.3.2.3 BADGE-2H_2O

A preliminary investigation was done to determine if a BADGE standard could cause chromatographic peaks with the LC/MS/MS bisphenol method. The resulting chromatograms are shown in Appendix Figure A.2.2.4 and after 7 days of contact time between BADGE and free chlorine, a peak was noted at 6.0 min. This is a similar retention time to BPA-like compound A. The experiment should be repeated at shorter time internals and without chlorine to determine if the BADGE standard is hydrolyzing to BADGE-2H_2O. A BADGE-2H_2O standard should also be investigated with the LC/MS/MS bisphenol method.

3.3.3 Mass Spec Investigation

Both LC and GC mass spectrometry were performed to more closely examine and compare the fragmentation patterns of BPA and BPA-like compound A. A stock solution of BPA-like compound A was generated by applying an epoxy coating to a 900-mL glass bottle, allowing the coating to cure for 24 hours, then filling the bottle with dechlorinated pH 8 tap water and holding it for 4 days at room temperature.

An LC/MS/MS product scan was conducted on *p,p´*-BPA, and three fragments were observed (Figure 3.3). The low number of fragmentation ions is attributable to BPA being a relatively small molecule and to negative mode electrospray producing less fragmentation than other ionization methods (i.e., electron impact). The product scan of BPA-like compound A also showed only three fragments: 212, 133, and 93, the same as for BPA. Additional LC/MS/MS

product scans would need to be done at higher m/z values to determine if the BPA-like peaks can be associated with BADGE-$2H_2O$, BAMGE-H_2O, or other similar compounds.

Electron-impact GC/MS scans compared the retention times and fragmentation patterns of an SPE-concentrated solution of *p,p'*-BPA and an SPE-concentrated solution of BPA-like compound A. The results showed that the retention times on the GC column were identical for *p,p'*-BPA and BPA-like compound A, and the mass spectra for the two compounds were virtually identical (Figure 3.4). This is important, as only subtle differences between BPA and BPA-like compound A would have caused different fragmentation patterns, since electron impact ionization breaks the linkage between the two bisphenol BPA rings. For example, even the *p,p'*-, *o,p'*-, and *o,o'*-BPA isomers can be differentiated through their GC fragmentation patterns.[47] Therefore, *p,p'*-BPA and BPA-like compound A appear to be structurally identical despite their different LC retention times.

3.3.4 Time-of-Flight

To further confirm the similarity of BPA and BPA-like compound A, LC/MS Time-of-Flight (TOF) MS was performed by the University of Kansas Mass Spectrometry & Analytical Proteomics Laboratory. TOF allows for measurement of an exact mass, sufficient for accurate determination of an analyte's elemental formula. The result of the TOF analysis was an exact mass match between BPA and BPA-like compound A (Table 3.4), further suggesting that BPA-like compound A is very similar to BPA, if not identical.

TOF provided an exact mass match for the three fragmentation ions of BPA and BPA-like compound A: 212, 133, and 93. This further corroborated the LC/MS/MS product ion scan (Figure 3.3) and MRM ions 212 and 133 that were confirmed with the BPA quantitation-to-

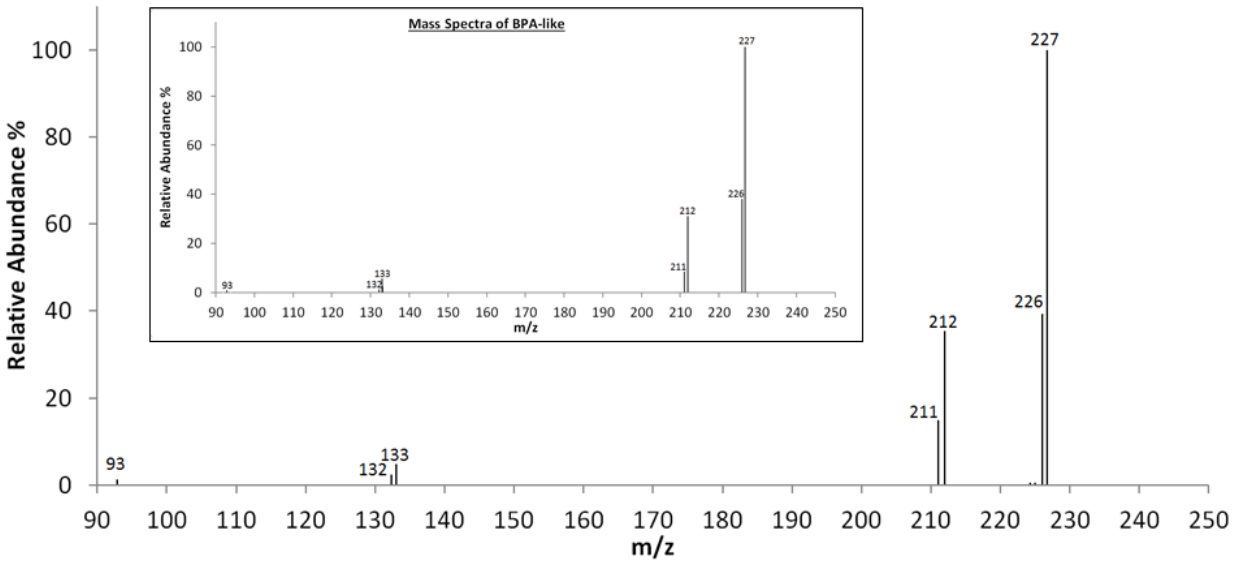


Figure 3.3 Mass spectrum from the LC/MS/MS product ion scan of a 20 µg/L BPA standard and inlay of the mass spectrum for BPA-like compound A.

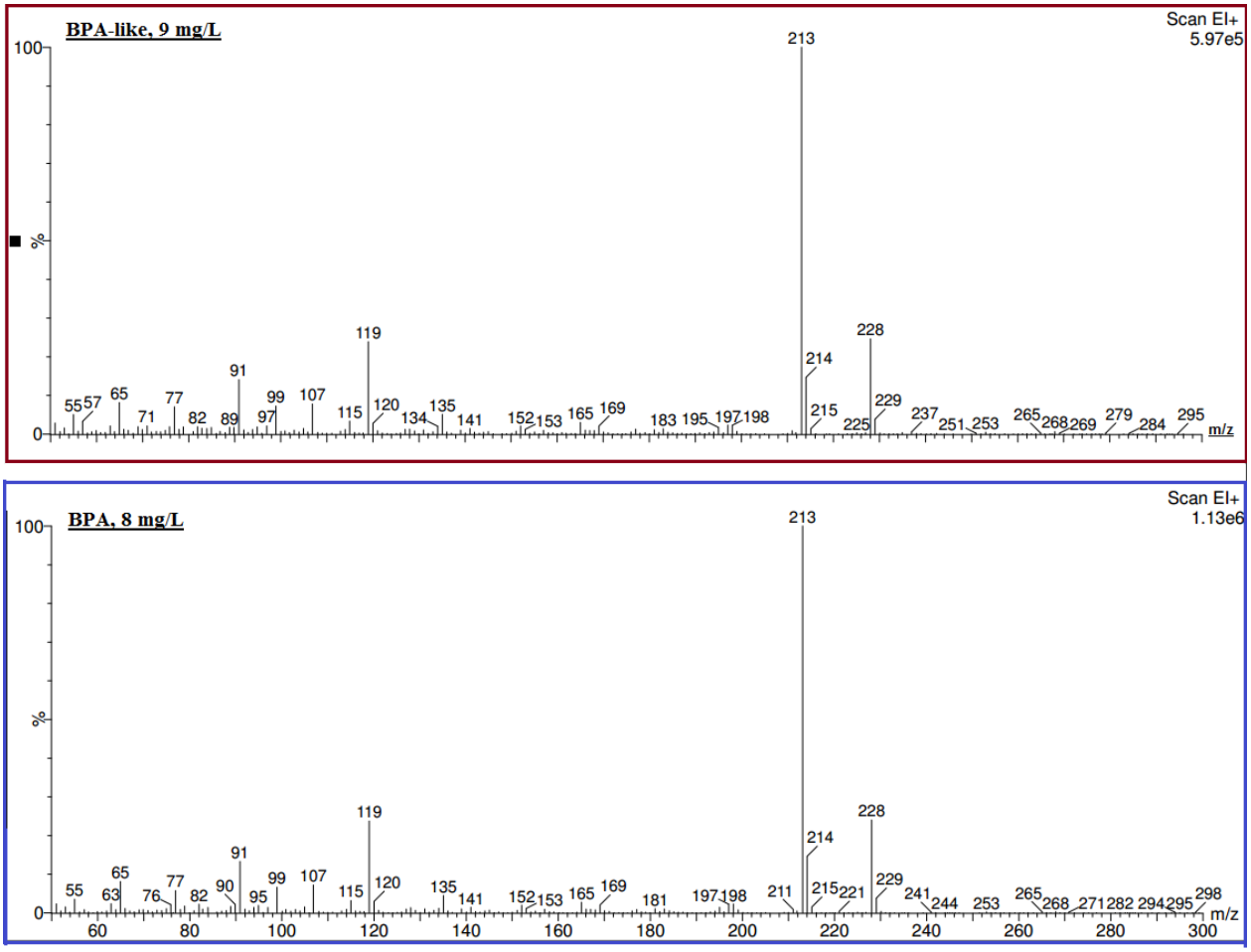


Figure 3.4 GC/MS mass spectrum for BPA-like compound A (SPE-concentrated to approximately 9 mg/L) compared to the mass spectrum for an 8 mg/L SPE-concentrated BPA standard.

Table 3.4 Time-of-Flight mass spectrometry data for an SPE-concentrated solution of p,p'-BPA and for an SPE-concentrated solution of BPA-like compound A. Data provided by the University of Kansas Mass Spectrometry & Analytical Proteomics Laboratory.

***p,p'*-BPA Standard**				**BPA-Like Compound A**		
Exact Mass Da	**Exact Mass Standard Deviation**	**Elemental Formula**		**Exact Mass Da**	**Exact Mass Standard Deviation**	**Elemental Formula**
227.1069	0.0009	$C_{15}H_{15}O_2$		227.1086	0.0016	$C_{15}H_{15}O_2$
212.0845	0.0013	$C_{14}H_{12}O_2$		212.0852	0.0011	$C_{14}H_{12}O_2$
133.0655	0.0058	C_9H_9O		133.0680	0.0020	C_9H_9O
93.0342	0.0018	C_6H_6O		93.0346	0.0004	C_6H_6O

confirmation-ion ratio. Since all the MS data indicated a high degree of structural similarity between BPA and BPA-like compound A, this reinforced our suspicion that the BPA-like compounds might be adducts of BPA.

3.3.5 Adduct Formation

Since BPA appeared to differ from BPA-like compound A only in its LC retention time, the possibility of adduct formation (or complexation) between BPA and a component of the epoxy or the extraction water was explored as a possible source of the BPA-like compounds. The hypothesis was that complexation may have occurred, forming adducts less hydrophobic than BPA (and therefore having shorter LC retention times than BPA), followed by dissociation of the adducts, either as they passed through the LC column or in the negative-mode electrospray ionization process, yielding detection of only BPA. Of all the potential complexing agents investigated in combination with BPA (Appendix Table A.2.1.1), the only one that exhibited a peak within the range of the retention times of the BPA-like compounds was TETA (Figure 3.5). The LC/MS/MS peak was relatively small and was observed only after 11 days of contact time. Binding of BPA to the secondary and tertiary amines of a supramolecule has been observed[48]; and cyclo-diBA, formed by the binding together of two BADGE molecules has been observed leaching into food products[49].

Although the two main starting materials in the epoxy used in this study were BADGE and TETA, other impurities and additives were present, and many other compounds were undoubtedly formed as the starting materials reacted to form an epoxy coating. The chromatogram of an SPE concentrated epoxy leachate solution containing the BPA-like compound A showed numerous other compounds present (Figure 3.6). It is possible that other

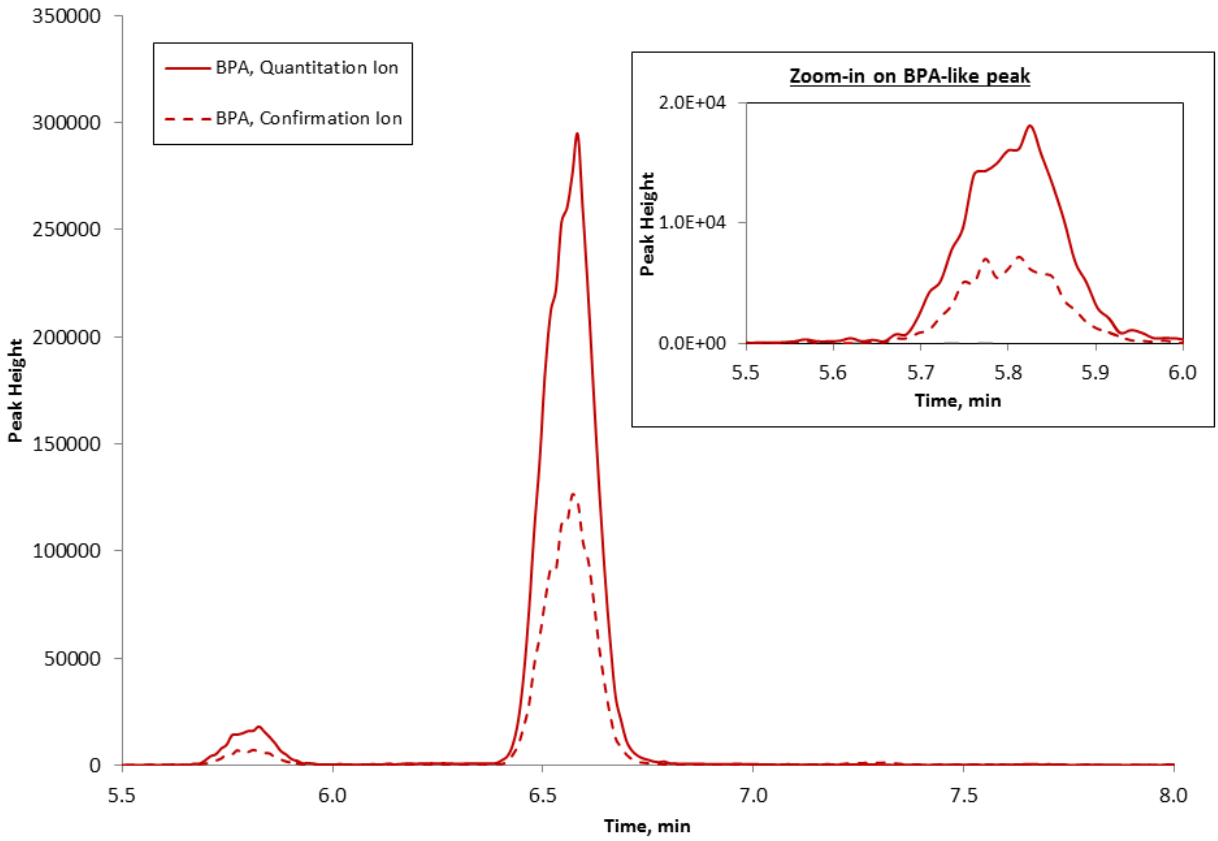


Figure 3.5 LC/MS/MS chromatogram for an 80 µg/L (0.00035 mM) BPA standard spiked into 20 mM TETA at pH 11 and held at room temperature for 11 days. The small peak at 5.8 min was not observed for earlier sampling times.

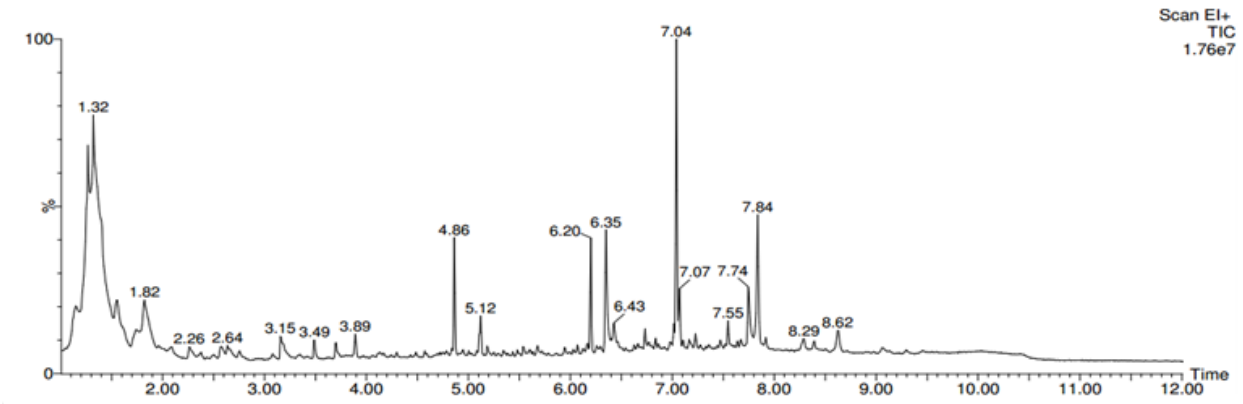


Figure 3.6 GC/MS chromatogram of a solution containing BPA-like compound A after concentration by solid phase extraction. Only the peak at 7.74 minutes had the same mass (228) as BPA.

compounds in the epoxy, besides the two main reactants, can form BPA adducts, giving rise to the spectrum of BPA-like compounds we observed. The effects on adduct yield of the stoichiometric ratio of BPA to TETA and other potential complexing agents were not explored (due to funding limitations), and it is possible that different ratios or other compounds might have resulted in higher yields of BPA-like compounds.

3.3.6 NMR

We considered using nuclear magnetic resonance (NMR) to further confirm the identity of BPA-like compound A, since NMR could provide additional structural information. Modern 2-dimensional (2-D) and 3-D NMR techniques provide information about the structural orientation of nuclei; proton NMR (^{1}H NMR), carbon-13 NMR (^{13}C NMR), and the Nuclear Overhauser Effect (NOE) have all been used to obtain structural information and differentiate between isomers of impurities in industrial grade BPA.[25] NMR chemical shifts, coupling constants, and peak multiplicities of ^{1}H and ^{13}C have provided structural information about halogen-related transformations of BPA.[50] A major limitation of NMR is that it requires large (mg) samples of the analyte and a relatively clean sample (as impurities in the sample significantly influence the quality of the NMR spectra).[51] These limitations prevented NMR analyses of the BPA-like compound A we generated; that is, the concentration (available mass) of BPA-like compound A was much too low for NMR and the solution was impure (Figure 3.6). Ackerman *et al*[38], through significant concentration and sample preparation steps, were able to use NMR data to aid in the identification of the BPA-like compounds observed in their study.

3.3.7 Stability

Four samples from FD1 containing BPA-like compounds A and B were reanalyzed 4 months after sample collection. During the 4 months, the samples were stored at 5 °C with the addition of 10% methanol. Upon reanalysis (Appendix Figures A.2.2.2 and A.2.2.3), there was an emergence of BPA, and changes in the peak heights of BPA-like compounds A and B were noted. In the chlorinated pH 8 extraction water samples, a BPA-like peak at 4.4 min was observed; this was similar to the 4.4 min peaks observed during FD2 (which also employed chlorinated pH 8 extraction water). The formation of this peak suggests the possibility that some of the minor BPA-like peaks are chlorinated adducts, for example, adducts formed with chlorinated polyamines, which could potentially react slowly with other constituents in solution and be dechlorinated over time. A chlorinated adduct would result in the BPA quantitation-to-confirmation-ion ratio not matching, and the ratios for minor BPA-like peaks did not always match (Table A.2.1.4).

The generated solution of BPA-like compound A remained stable throughout the two-month period during which during it was subjected to LC/MS/MS, GC/MS, and LC/TOF/MS analyses. Therefore, the results of these analyses are not attributable to degradation of BPA-like compound A to BPA during sample storage.

3.4 Conclusions

Based on the results presented herein, the BPA-like compounds observed are potentially BADGE hydrolysis products or BPA adducts that after ionization behave as BPA. A sample presumed to have BADGE-$2H_2O$ was found to produce a peak at the same retention time as the BPA-like compound A. However, no correlation was found between the BADGE-

$2H_2O$ and BPA-like compound A during the fill-and-dump sampling and more than two BPA-like peaks were observed. The complexation study between BPA and TETA resulted in a small chromatographic peak at 5.8 min and adduct formation could be the cause of the small peaks. Additional LC/MS/MS chromatograms and scans must be collected to differentiate between BADGE hydrolysis products mimics and adducts. The implications of this are that retention times surrounding BPA should also be considered when analyzing samples for BPA and related compounds; otherwise, compounds could be overlooked in studies addressing the occurrence, transformations, or fate of BPA.

3.5 References

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Chapter 4: Bisphenol Diglycidyl Ethers and Bisphenol A and Their Hydrolysis in Drinking Water

Lane, R.F.; Adams, C.D.; Randtke, S.J.; Carter, Jr. R.E. Bisphenol diglycidyl ethers and bisphenol A and their hydrolysis in drinking water. *Water Res* **2015,** *72*, 331-9.

4.1 Introduction

Bisphenol A (BPA) has been reported to leach from plastics and epoxy coatings into a wide variety of foods and beverages[1,2] resulting in the detection of BPA in various human tissues and fluids[3]. BPA is a xenoestrogen and animal studies have shown negative effects on the prostate, immune system, and mammary glands, as well as on reproduction, brain development and functioning, metabolism, and migraine symptoms.[4,5] Human studies have examined elevated levels of BPA in regards to reproduction, neurobehavioral development, and metabolic diseases (e.g. obesity, diabetus, heart diesease, thyroid and liver function).[6] While this research demonstrated elevated BPA levels could be correlated with negative human impacts, causality was not proven. The U.S. Environmental Protection Agency and U.S. Food and Drug Administration (FDA) have considered regulating BPA but decided not to regulate based on lack of scientific evidence of adverse human health effects at low levels of exposure.[7,8] Both organizations have committed to reviewing new information as it becomes available and taking additional action if it is warranted.

Although there are no pending regulations, there has been public concern in recent years over the use of BPA (especially in baby bottles). Public concerns about BPA exposure are leading manufacturers to consider other bisphenols (such as bisphenol B, bisphenol D, bisphenol E, or bisphenol F) for use in epoxy and plastics.[9,10] One such common alternative is bisphenol F (BPF) which is structurally similar to BPA (Figure 4.1). BPF has been detected in the environment and food products but to a lesser extent than BPA.[11,12] One study suggests BPF

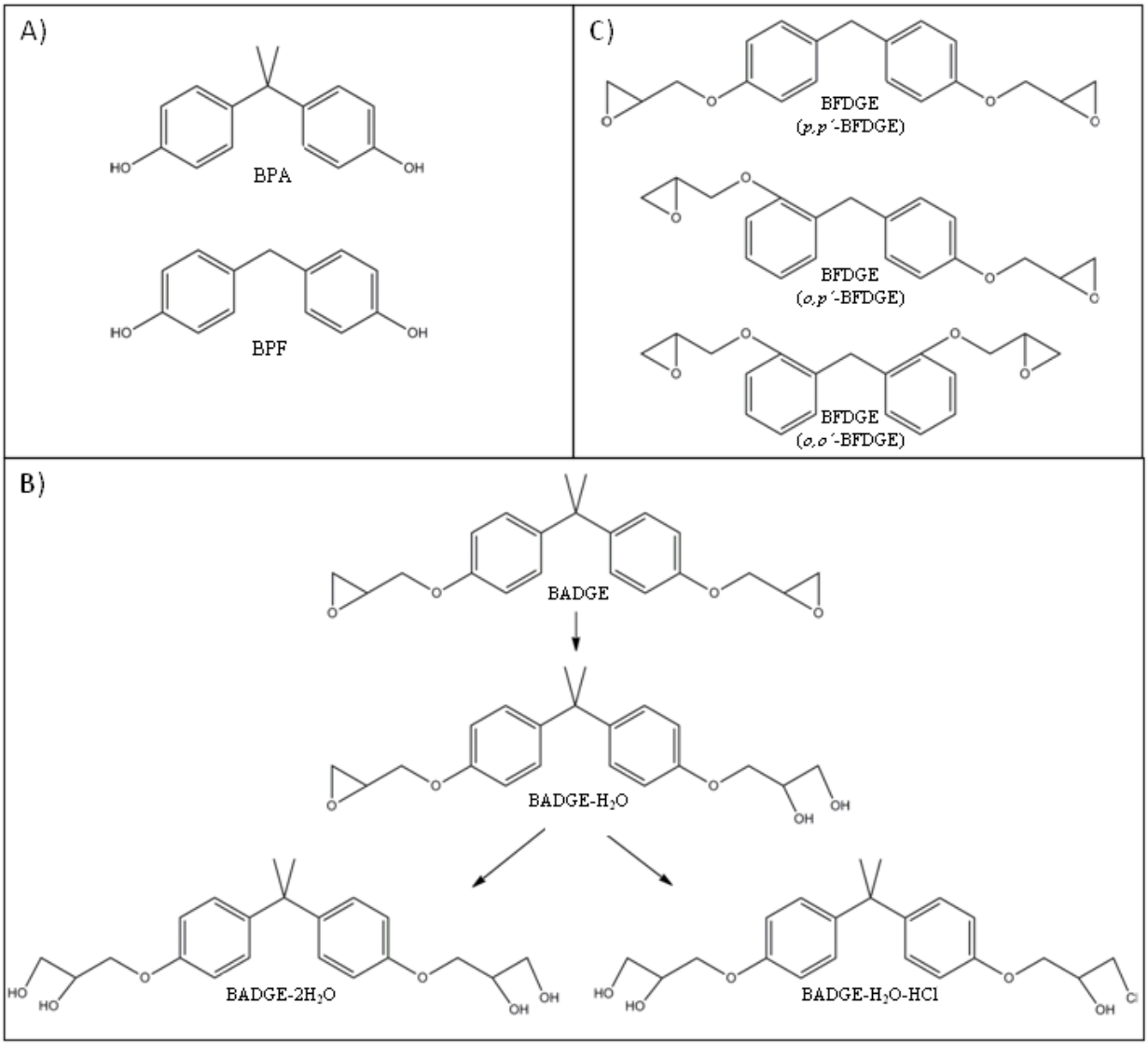

Figure 4.1 Chemical structures of key analytes. A) Structures of two epoxy starting materials bisphenol A (BPA) and bisphenol F (BPF). B) Epoxy prepolymer bisphenol A diglycidyl ether (BADGE) and three hydrolysis products BADGE-H_2O, BADGE-$2H_2O$, BADGE-$2H_2O$-HCl. C) Epoxy prepolymer bisphenol F diglycidyl ether (BFDGE or *p,p'*-BFDGE) and two common isomers, *o,p'*-BFDGE and *o,o'*-BFDGE.

also has estrogenicity but to a lesser degree than BPA[13]. This lower estrogenicity may be due to the fact that estrogen receptor binding is influenced by the overall length of the hydroxylated chains and bridging carbons.[14,15]

As with food cans, epoxy coatings can be used to prevent leaching of metals, especially lead and copper, from water service lines into drinking water. The EPA's Lead and Copper Rule established action levels of 15 µg/L (or parts-per-billon, ppb) for lead and 1,300 µg/L for copper.[16] If these levels are exceeded in a given percentage of samples, a utility must take steps to lower them. One control option is lead service line replacement. Replacement can be challenging and costly, so this has generated interest in lining and coating technologies as an alternative to replacement. Epoxy coatings are commonly used to protect the interior (and exterior) surfaces of water mains and can be used on the interior surfaces of water pipes in homes, hospitals, hotels, and other buildings.

Epoxy coatings for potable water are often formed from two starting materials: a resin and a hardener. The resin prepolymer is designed to facilitate polymerization and is often a bisphenol with reactive epoxide side chains.[17] Common prepolymers are bisphenol A diglycidyl ether (BADGE) or bisphenol F diglycidyl ether (BFDGE), with BPA and BPF as the respective bisphenol starting materials. After the resin and a hardener (typically a polyamine) are mixed and cured, any remaining starting materials have the potential to leach into the drinking water.

Monitoring of starting materials is limited but studies have reported BADGE and BFDGE in food products[18-20] and the environment[21]. Further, a recent study found a correlation between the detection of BPA and the detection of BADGE in urine.[22] Due to concerns over mutagenicity[23,24], genotoxicity[23,24], and anti-androgenicity[25], the European Union has

established a 9 mg/kg food migration limit for BADGE and its hydrolysis products[26]. BADGE and BFDGE have several hydrolysis products and kinetic modeling has been done to predict decay in food products.[27-30] There are currently no kinetic models describing hydrolysis kinetics in drinking water systems, and the kinetic studies in food were performed at elevated temperature (from 40 to 60 °C).

The use of epoxies in small-diameter pipes (such as water service lines), which have relatively high ratios of surface area to volume and flow intermittently, maximizes the potential for organic chemicals to leach into drinking water, representing a worst-case scenario for human exposure to epoxy leachates in drinking water. The purpose of this study is to provide data and hydrolysis models to support assessments, by others, of human exposure to BADGE, BFDGE, and BPA and their hydrolysis products. The objectives were to determine the primary organic leachates from a potable-water-grade epoxy, identify their hydrolysis products, and develop a hydrolysis model to predict concentrations of leachates and their hydrolysis products in drinking water over time.

4.2 Materials and Methods

4.2.1 Reagents and Chemicals

Potable-water-grade epoxy was obtained from a manufacturer who also applied epoxy coatings to lead and copper pipe specimens as described below. Part A of the two-part epoxy consisted of the resin prepolymer (including BADGE), while Part B was the hardener (including a polyfunctional triethylenetetramine (TETA)). All water was treated by a Millipore Elix Reverse Osmosis system followed by a Millipore A10 unit. Tap water was collected after allowing the water tap to run for at least 5 min prior to collection. LC/MS grade methanol (Optima),

monobasic and dibasic sodium phosphate, and sodium bisulfite were purchased from Fisher Scientific (Pittsburgh, PA). Ammonium formate and formic acid were purchased from Sigma Aldrich (St. Louis, MO). Bisphenols (BPA, BPB, BPD, BPE, and BPF) were purchased from TCI America (Portland, OR). The diglycidyl ether compounds (BADGE, BADGE-H_2O, BADGE-$2H_2O$, BADGE-H_2O-HCl) were purchased from Sigma Aldrich (St. Louis, MO), while BFDGE was purchased from Crescent Chemical Co. (Islandia, NY). Internal standards, BPA-D8 and SMXL-D4 (sulfamethoxazole-D4), were ordered from Cambridge Isotopes Laboratory (Tewksbury, MA) and Toronto Research Company (Toronto, Ontario, Canada), respectively. Chemical structures of the analytes are shown in Figure 4.1 and Table A.3.1.2.

4.2.2 Analytical Methods

Liquid chromatography – mass spectrometry (LC/MS/MS) methods for detection of bisphenols and diglycidyl ether compounds were adapted from previously described methods[9,31]. The LC system consisted of a Shimadzu (Columbia, MD) Prominence High Performance LC (HPLC) equipped with a LC-20AB binary pump, DGU-20A3 degasser, and SIL-20A autosampler. Chromatographic separation was obtained with a reverse phase Gemini-NX C18-with-TMS-endcapping column, 150 × 3.0 mm, 3-micron particle size (Phenomenex, Torrance, CA), at a flow rate of 0.4 mL/min. The mobile phase for the bisphenols was water and methanol, while the mobile phase for diglycidyl ethers was 25 mM ammonium formate at pH 3.75 and methanol. During bisphenol analysis, a 50 µL aliquot was injected and the gradient was applied as follows: methanol was ramped from 65% to 85% over 5 min, held at 85% for 6 min, ramped from 85% to 100% over 3 min, held at 100% for 2 min, then returned to 65% over 4 min and held for 5 min. For the diglycidyl ethers, a 50 µL aliquot was injected and the gradient

was applied as follows: methanol was ramped from 30% to 60% over 4.5 min, then from 60% to 84% over 5 min, from 84% to 90% over 10 min, from 90% to 100% over 5 min, held at 100% for 2 min, and then returned to 60% over 5 min.

A 4000 QTrap triple-quadrupole linear ion-trap mass spectrometer with a turbo ion-spray source (AB SciEx, Framingham, MA) was used for detection. The electrospray source was operated with nitrogen gas for nebulization. The MS/MS parameters were optimized for each analyte and are summarized in Table 4.1 (and Appendix Table A.3.1.2). BPA-D8 was selected as the internal standard for the bisphenols, and SMXL-D4 as the diglycidyl ether internal standard. Method detection limits (MDL) were determined as outlined in *Standard Methods*[32].

Gas chromatography MS (GC/MS) was used to scan for potential epoxy leachates. An Agilent (Agilent Technologies, Santa Clara, CA) 6890A GC with Agilent 5973N MS operated in scan mode was used with a 7683 autosampler and HP-5MS 0.25 mm ID x 30 m column with a 0.25-µm film thickness. Additional information provided in Appendix Table A.3.1.1. The epoxy was prepared for GC/MS by dissolving 1 gram of each component in 10 mL of methanol. Prior to injection the solutions were further diluted with methanol by a factor of 1:150.

4.2.3 Pipe Samples

Epoxy was applied by the manufacturer to 1.59-cm internal diameter Pb and Cu water service lines, cured for 48 hours, and then flushed for 15 min with cold tap water to remove any particles or readily dissolved materials from the surface of the coating.[33] The pipes were filled with one of three extraction waters (pH 8 dechlorinated tap water, pH 8 chlorinated reagent water, or pH 6 dechlorinated reagent water) and held at 20 °C for 6 h, 24 h, 96 h, and 10

Table 4.1 LC/MS method parameters and method detection limits (MDLs).

Compound	CAS Number	MS Ionization Mode	Precursor Ion m/z		Product Ion, m/z	Declustering Potential (V)	Collision Energy (V)	Collision Cell Exit Potential (V)	MDL (µg/L)
BPA	80-05-7	negative	**[M-H]⁻**	**227.0**	**212.0**	-76.020	-24.870	-3.120	0.057
			[M-H]⁻	227.0	133.0	-76.020	-31.260	-10.350	
BPA-D8	92739-58-7	negative	**[M-H]⁻**	**235.0**	**220.0**	-76.200	-25.680	-4.580	NA
			[M-H]⁻	235.0	137.0	-78.040	-35.620	-8.860	
BPF	77-40-7	negative	**[M-H]⁻**	**199.0**	**93.0**	-67.190	-29.070	-6.880	0.18
			[M-H]⁻	199.0	105.0	-70.680	-28.420	-5.560	
BADGE	1675-54-3	positive	**[M+NH4]⁺**	**358.2**	**191.0**	51.950	21.490	12.040	7.0
			[M+NH4]⁺	358.2	135.0	51.950	43.410	7.610	
BADGE-H_2O	76002-91-0	positive	**[M+NH4]⁺**	**376.4**	**209.0**	46.490	20.470	12.370	1.5
			[M+NH4]⁺	376.4	135.0	46.490	40.380	6.460	
BADGE-$2H_2O$	5581-32-8	positive	**[M+NH4]⁺**	**394.4**	**209.0**	46.870	23.710	12.240	1.4
			[M+NH4]⁺	394.4	135.0	46.870	46.160	6.320	
BADGE-H_2O-HCl	227947-06-0	positive	**[M+NH4]⁺**	**412.8**	**135.0**	38.500	48.570	6.110	7.6
			[M+NH4]⁺	412.8	227.1	38.500	21.930	13.800	
BFDGE	2095-03-6	positive	**[M+NH4]⁺**	**328.8**	**163.0**	41.970	19.350	8.930	0.24
			[M+NH4]⁺	328.8	133.0	42.960	24.330	6.350	
SMXL-D4	1020719-86-1	positive	**[M+H]⁺**	**258.0**	**96.0**	56.360	45.250	17.080	NA
			[M+H]⁺	258.0	112.0	72.140	35.410	5.620	

transitions in bold are quantitation ions NA = Not Applicable

days.[33,34] Tap water was dechlorinated with sodium bisulfite and tested with HACH Total Chlorine Method 8167 (USEPA DPD Method) to confirm chlorine removal.

4.2.4 Hydrolysis

Hydrolysis studies of BADGE, BFDGE, and bisphenols were carried out based on a pseudo-first-order kinetic approach. Analytes were spiked into 5 mM phosphate buffer at pH values of 2-12 at reaction temperatures of 5, 15, 25, and 40 °C. Hydrolysis of BFDGE was monitored only at 25 °C, for comparison to BADGE. The pH was monitored at the beginning, middle, and end of experiments, with the mean and median drift in pH being only 0.3 and 0.1 pH units.

4.3 Results and Discussion

4.3.1 Key Bisphenol Leachates

This study focused on key bisphenol leachates and their hydrolysis products, that is, selected bisphenol compounds present in the starting materials or formed later that may leach into water in concentrations high enough to be of significant public health or regulatory concern. The study did not focus on non-bisphenol compounds (e.g., polyamines) or on trace impurities. To determine possible bisphenol leachates in the epoxy starting materials, a GC/MS scan was performed on the proprietary part A and part B epoxy components. BADGE was identified in part A using the National Institute of Standards and Technology (NIST) spectral library (Figure 4.2). BFDGE, BPA, and other bisphenols were not detected in the starting materials.

The key bisphenol leachate identified in the highest concentrations in water samples from fill-and-dump tests on epoxy-coated pipe specimens was BADGE (Appendix Table A.3.1.3).

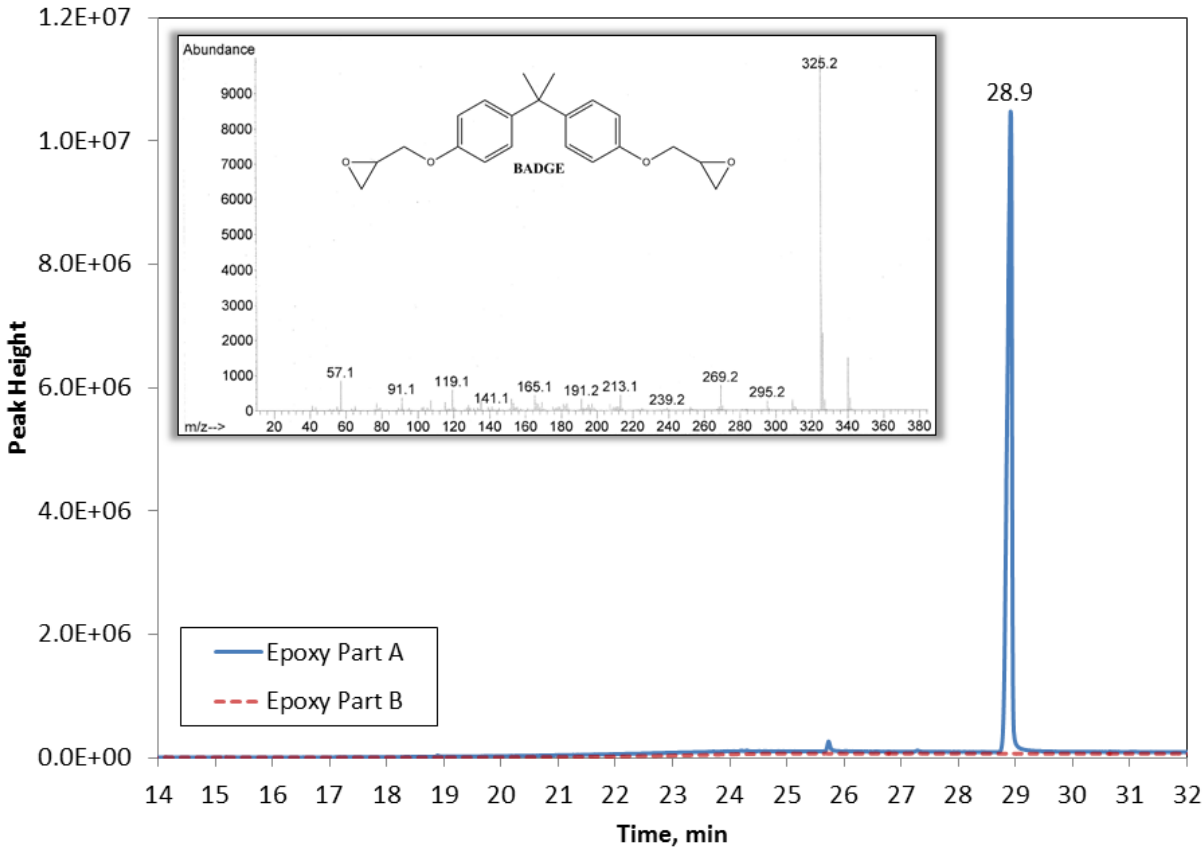

Figure 4.2 GC/MS chromatogram from a scan of epoxy components A and B. The mass spectra is shown for the peak at 28.9 minutes and was matched with the NIST spectral library to BADGE.

The samples were also tested for BPA, BPB, BPD, BPE, and BPF. None of these bisphenols were observed based on consistent mass spectra and retention time in comparison to standards. Another bisphenol compound, hypothesized to be a BPA adduct, was detected in some samples at concentrations high enough to be considered a key leachate. This compound was not identified with certainty and its hydrolysis was not studied. Because of potential interest not only to the drinking water community, but also to food chemists and others, the compound's behavior and evidence for its structure will be discussed in a separate publication.

The highest BADGE concentrations observed in the pH 8 extraction waters were approximately 240 µg/L after holding times of 6 to 24 hours. No detectable BADGE was found in samples held 4 or 10 days, or in the pH 6 extraction water. It is hypothesized (based on results presented below) that BADGE decayed via hydrolysis in the samples. BFDGE was not analyzed for since a BADGE-based epoxy was used; but BFDGE is very similar to BADGE and small amounts of BFDGE would also be expected to leach into drinking water from a freshly applied coating of a BFDGE-based epoxy.

4.3.2 The Hydrolysis Model

Modeling the hydrolysis rate as a function of pH (2-12) and temperature (15, 25, and 40 °C) allows prediction of compound degradation and occurrence for a range of scenarios. Experimental modeling was attempted at 5 °C but the experimental results were erratic, due possibly to significant analyte sorption to the glass vials at a lower temperature.

The hydrolysis model was derived assuming pseudo-first-order kinetics, with the decay of BADGE described by:

$$\text{BADGE} \xrightarrow[\text{hydrolysis}]{} \text{products} \quad (1)$$

$$\frac{d\text{BADGE}}{dt} = -k_A[\text{BADGE}][\text{H}^+] - k_N[\text{BADGE}] - k_B[\text{BADGE}][\text{OH}^-] \quad (2)$$

The kinetic rate terms for acidic hydrolysis (k_A, $M^{-1}s^{-1}$), neutral hydrolysis (k_N, s^{-1}), and basic hydrolysis (k_B, $M^{-1}s^{-1}$) can be incorporated into a single rate term (k'_{Hyd}):

$$\frac{d\text{BADGE}}{dt} = -(k_A[\text{H}^+] + k_N + k_B[\text{OH}^-])[\text{BADGE}] = -\text{k}'_{\text{Hyd}}[\text{BADGE}] \quad (3)$$

Separation and integration provides:

$$\ln\left(\frac{[\text{BADGE}]}{[\text{BADGE}]_0}\right) = -\text{k}'_{\text{Hyd}}\text{t} \quad (4)$$

First order plots were generated over time (t) to determine an experimental rate constant k'_{Hyd} (Appendix Table A.3.1.4 and Table A.3.1.5).

The model was also developed and calibrated experimentally for BFDGE at 25 °C. BFDGE is only commercially available as an isomeric mix (i.e., *o,o'*-BFDGE, *o,p'*-BFDGE, *p,p'*-BFDGE). Pseudo-first-order rates constants for BFDGE were determined for each isomer as a function of pH (Appendix Table A.3.1.6). The relative standard deviations (%RSD) between duplicates for the three isomers ranged from 8 to 31%. There were significant differences ($\alpha \leq 0.05$) only at pH 7.17 and 11.56. For modeling purposes, the pseudo-first-order rate constants were combined to develop an overall averaged kinetic rate model.

At each temperature studied, non-linear, least-squares regression using MS Excel was the basis for determination of the BADGE and BFDGE acidic, neutral, and basic rate constants (Table 4.2). The effect of temperature on the three rate constants (i.e., k_A, k_N and k_B) was

modeled using the Arrhenius approach, Figure 4.3. The experimental results followed the theoretical model closely at 15, 25, and 40 °C.

As illustrated in Figure 4.4, the model appears to effectively predict experimental results. Further, it can be seen that the hydrolysis rates of BADGE and BFDGE were nearly identical, as might be expected based on their structural similarity (Figure 4.1).

The resulting model for BADGE hydrolysis, including both pH and temperature effects (Equations 5), is:

$$\ln\left(\frac{[\mathrm{BADGE}]}{[\mathrm{BADGE}]_0}\right) = -\left[(k_A 10^{-\mathrm{pH}}) + k_N + \left(\frac{k_B 10^{\log \mathrm{Kw}}}{10^{-\mathrm{pH}}}\right)\right]\mathrm{t} \quad (5)$$

where:

$$\log \mathrm{K_W} = -\left(\frac{4470.99}{\mathrm{T(K)}}\right) + 6.0875 - (0.01706 \times \mathrm{T(K)}) \quad (6)$$

$$k_A = e^{(-8{,}547 \cdot (1/\mathrm{T(K)}) + 23.16)} \quad (7)$$

$$k_N = {}^{(-7{,}547 \cdot (1/\mathrm{T(K)}) + 12.05)} \quad (8)$$

$$k_B = e^{(-10{,}358 \cdot (1/\mathrm{T(K)}) + 27.05)} \quad (9)$$

The half-life of BADGE is calculated according the Equation 10 and is plotted in Figure 4.5.

$$\text{Half life (days)} = \frac{-\ln(0.5)}{k'_{\mathrm{Hyd}}} \quad (10)$$

The half-life of BADGE in 40 °C distilled water has previously been reported in the literature at 1.8[29], 1.7[27], and 1.3[30] days. Our model is in relatively good agreement (e.g., 1.4 days at pH 7 and 40 °C). From work in the food packaging industry, the half-life of BFDGE in 40 °C distilled water was reported as 2.1 days[28]. Our longer BFDGE half-life is due to a 15 °C colder temperature. For example, the half- lives of BADGE at pH 7 and 15, 25, 35, and 40 °C are 11, 4.6, 2.0, and 1.4 days, respectively.

Table 4.2 Experimentally determined rate constants for BADGE and BFDGE.

Analyte	Temperature	k_A ($s^{-1}M^{-1}$)	k_N (s^{-1})	k_B ($s^{-1}M^{-1}$)
BADGE	15 °C	1.52E-03	7.02E-07	1.57E-04
BADGE	25 °C	3.99E-03	1.85E-06	3.64E-04
BADGE	40 °C	1.61E-02	5.73E-06	2.67E-03
BFDGE*	25 °C	5.03E-03	1.60E-06	1.47E-04

* Rate constants shown for BFDGE are averages for three isomers.

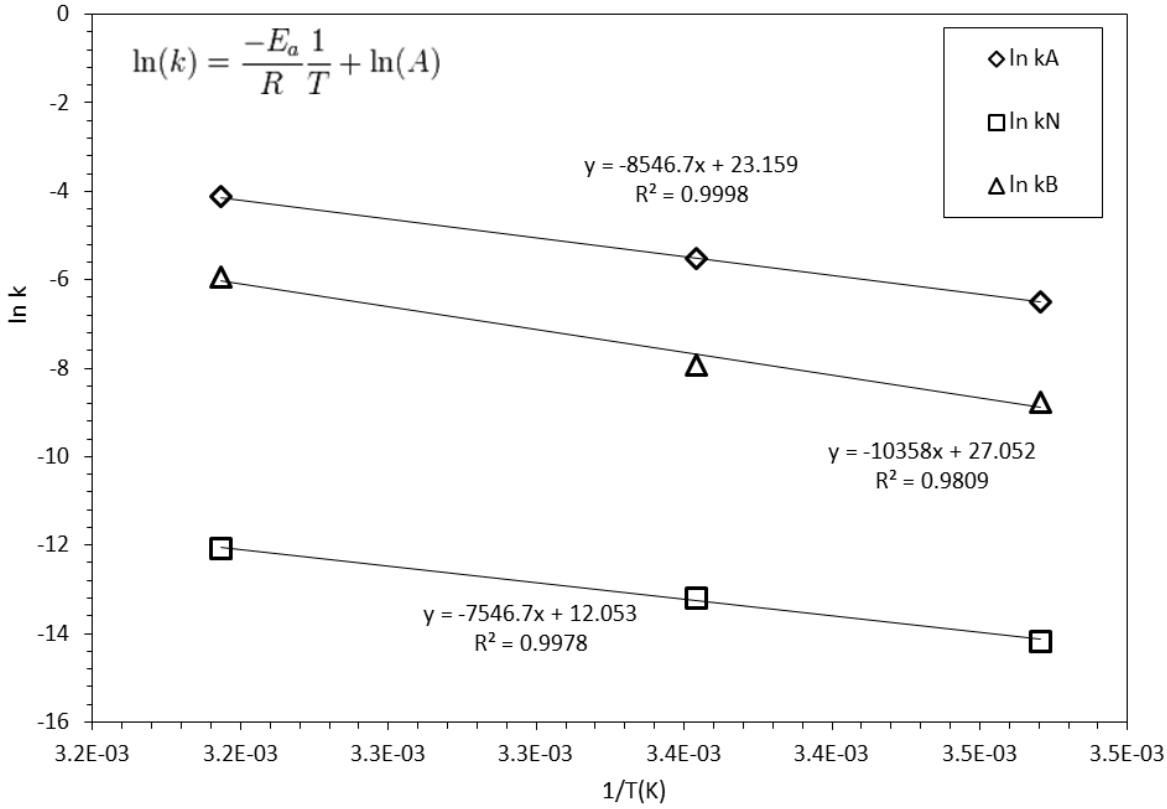

Figure 4.3 Arrhenius plot for the hydrolysis of BADGE.

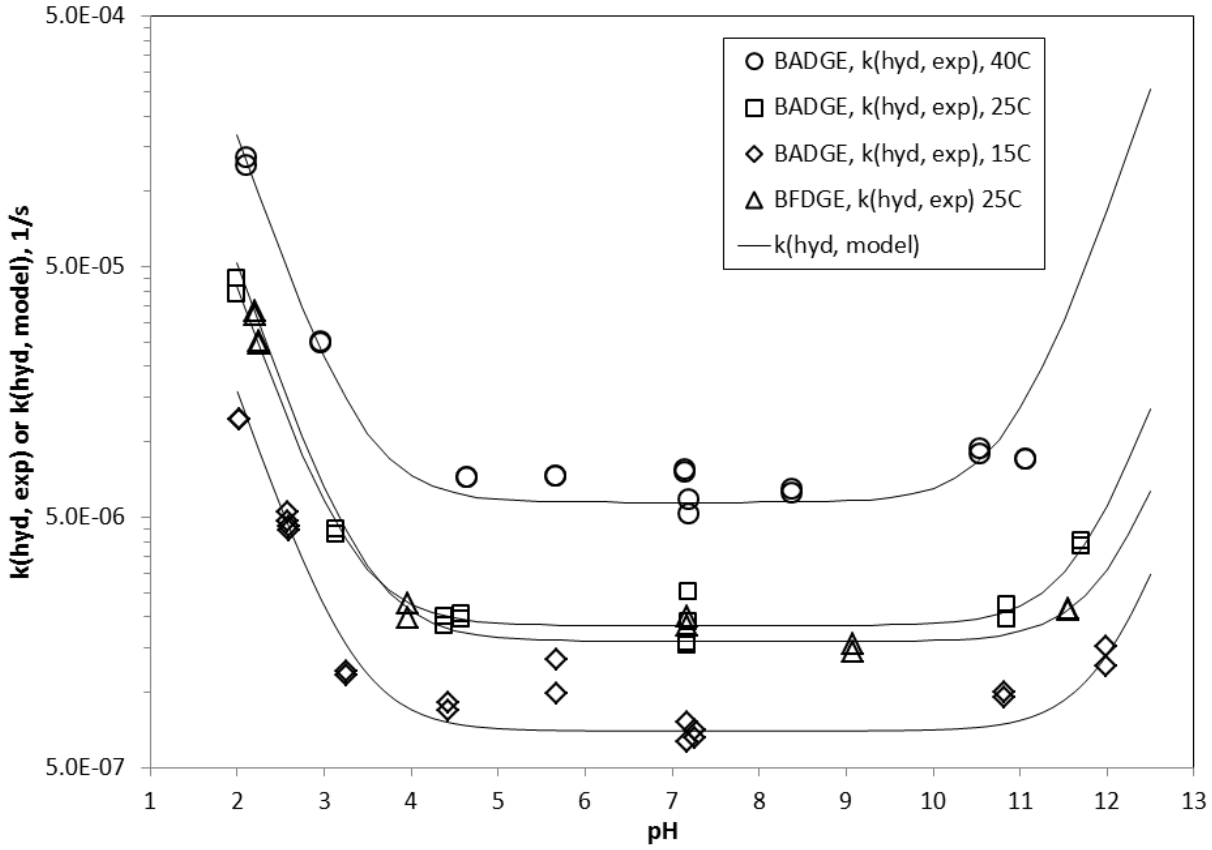

Figure 4.4 Plot comparing the experimental kinetic rate values (data points) and model results (black lines). BADGE was modeled at 15, 25, and 40 °C, and BFGDE was modeled at 25 °C for comparison.

The half-lives of BADGE were calculated based on the developed model for pH values of 2-12 and temperatures of 15-40 °C. It may be seen (Figure 4.5) that the half-lives range from less than 2 days at 35 °C to nearly 11 days at 15 °C. This is highly relevant with respect to human exposures to the parent compounds. Residence times of less than two days may occur in various portions of household plumbing on a regular basis, while residence times of 11 days would be less frequent except, for example, during vacations or for infrequently used taps.

4.3.3 Hydrolysis Products

Selected hydrolysis products (BADGE-H_2O, BADGE-$2H_2O$, BADGE-H_2O-HCl) were monitored during BADGE hydrolysis experiments. Regardless of the temperature, the following trend was observed (Figure 4.6): a steady decay of BADGE, an initial increase and then decrease of BADGE-H_2O, and a slow steady increase in the concentration of the final product BADGE-$2H_2O$. Other potential hydrolysis product, BADGE-H_2O-HCl, was not observed (as consistent with experimental conditions not promoting the addition of chlorine to the epoxide). The reactions of BADGE with free and combined chlorine are being examined in a separate study, the results of which have not yet been published.

4.3.4 BPA Hydrolysis

The hydrolysis of BPA was also tested, at temperatures of 25 and 40 °C and pH 2 to 12. Significantly, no hydrolysis or decay of BPA was observed up to reaction times of 30 days (Appendix Figure A.3.2.1). This was also expected, as BPA does not have readily hydrolysable groups as does BADGE and BFDGE (with their epoxide functionalities).

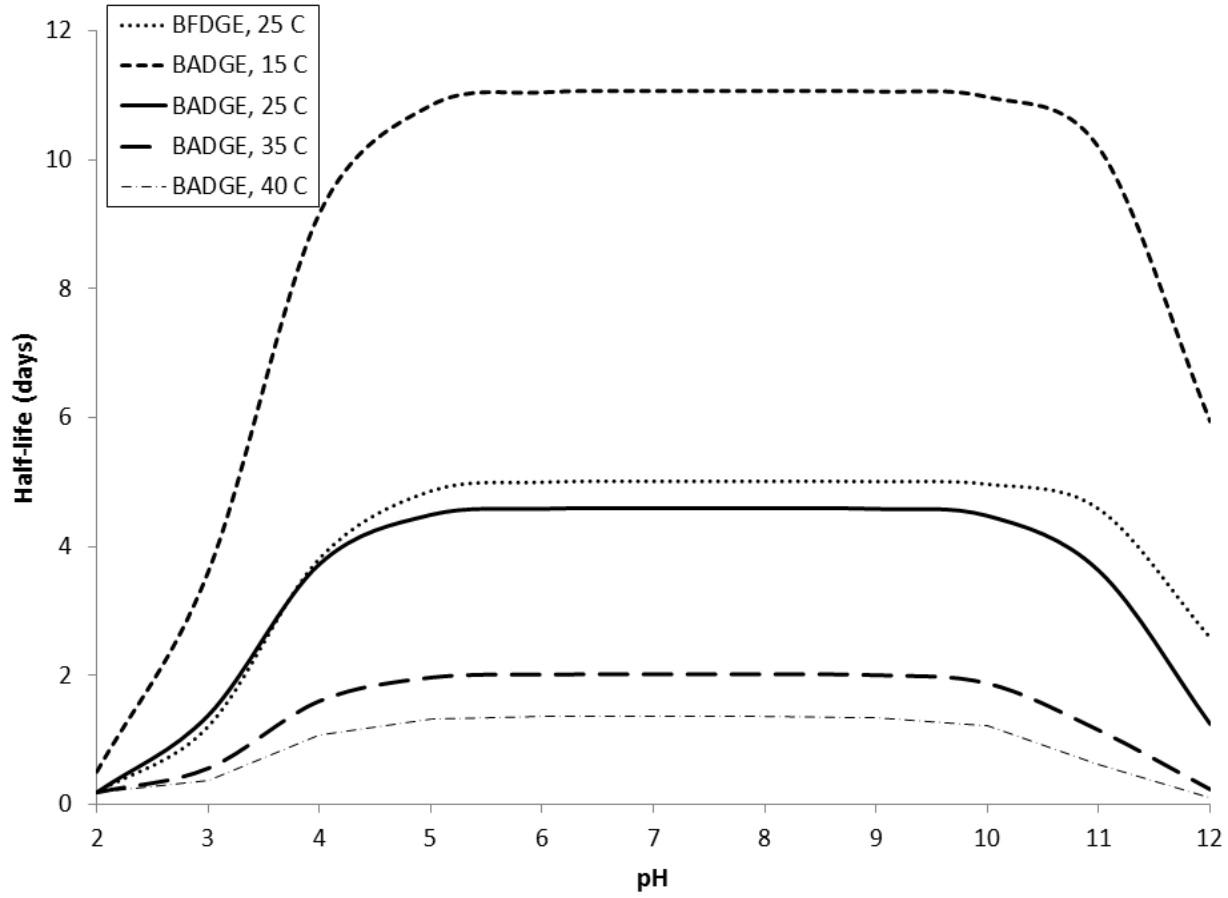

Figure 4.5 Modeled half-lives of BADGE and BFDGE at 15, 25, 35, and 40 °C in phosphate-buffered waters.

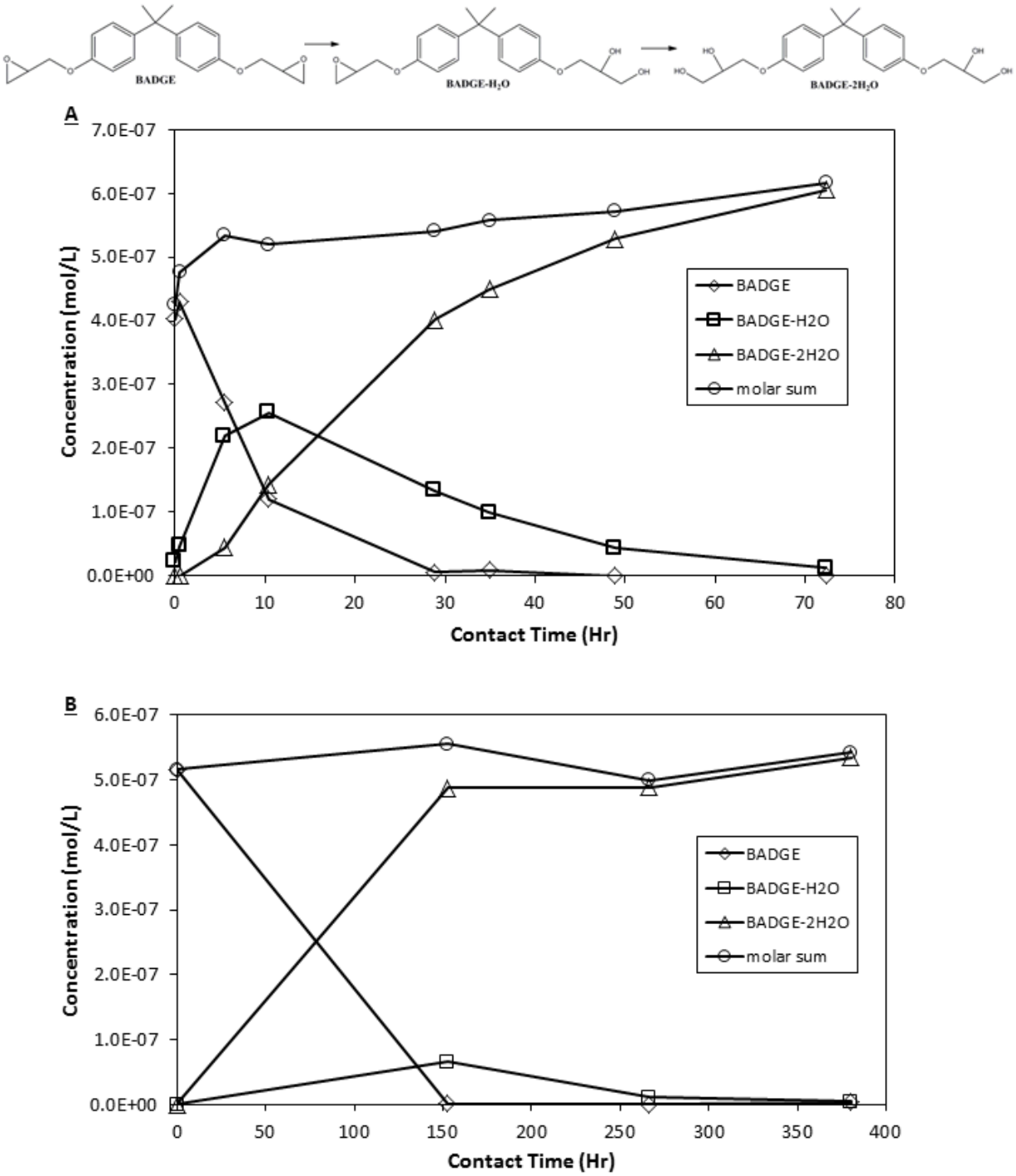

Figure 4.6 Formation of BADGE hydrolysis products: plot A is for pH 2 at 25 °C and plot B is for pH 2 at 40 °C. Steady decay of BADGE was noted, followed by an increase and decrease of BADGE-H2O, and steady increase in the final product, BADGE-2H2O.

4.4 Conclusions

BADGE and a BPA-like compound were identified as leachates from a BADGE-based epoxy used to coat lead and copper pipe specimens. BPA and other bisphenols were not detected. Based on experimental data, BADGE hydrolysis was modeled at pH values of 2–12 and temperatures of 15–40 °C, and BFDGE hydrolysis was modeled at pH values of 2–12 at 25 °C. The hydrolysis rates of both BADGE and BFDGE were relatively constant at pH values of 5–10, but increased significantly at higher and lower pH values; that is, their hydrolysis is both acid and base catalyzed. The hydrolysis model predicts BADGE half-lives at pH 7 and 15, 25, 35, and 40 °C to be 11, 4.6, 2.0, and 1.4 days respectively; the BFDGE half-life is predicted to be 5 days at pH 7 and 25 °C. BPA was not observed to hydrolyze in 30 days at pH values of 2 to 12 and temperatures of 25 and 40 °C. Identified BADGE hydrolysis products included BADGE-H_2O and BADGE-$2H_2O$, with BADGE-$2H_2O$ being the final end product under the time, temperature, and pH conditions studied, which encompass conditions representative of those encountered in drinking water distribution systems.

4.5 References

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Chapter 5: Chlorination and Chloramination of Bisphenol A, Bisphenol F, and Bisphenol A Diglycidyl Ether in Drinking Water

Lane, R.F.; Adams, C.D.; Randtke, S.J.; Carter, Jr. R.E. Bisphenol diglycidyl ethers and bisphenol A and their hydrolysis in drinking water. *Water Res* **2015,** In press.

5.1 Introduction

Bisphenol A (BPA) is a compound frequently used in epoxy resins and polycarbonate plastics. Epoxy resins can be used to coat the inside of food cans, water storage tanks, water mains, and water service lines, while polycarbonates are used in a wide variety of applications.[1] In manufacturing epoxy resins, BPA is reacted with an epichlorohydrin to form a reactive prepolymer, bisphenol A diglycidyl ether (BADGE). Consumers have expressed concerns about the estrogenic properties of BPA and manufactures reportedly are seeking structurally similar compounds, such as bisphenol F (BPF), as BPA replacements.[2] Despite its elimination from some products, such as baby bottles[3], BPA is still widely used in manufacturing epoxies and plastics[4].

Leaching of BPA from epoxies and plastics has been reported in a wide variety of foods[5-7], beverages[6], and drinking water[8,9]. In the case of drinking water, BPA can leach from epoxy coatings used to protect against corrosion, especially when water is left standing in the service lines.[8,9] BPA has also been detected in the part-per-trillion (ng/L) to part-per-billion (µg/L) range in many bodies of water that serve as drinking water sources.[10-12] Although less extensively studied than BPA, BADGE and BPF have also been detected in foods[2,13-15] and water[16,17]. BPA is a xenoestrogen and studies have examined correlations between elevated levels of BPA and negative impacts on reproduction, neurobehavioral development, and metabolic diseases

(e.g. obesity, diabetes, heart disease, thyroid and liver function).[18] The U.S. Environmental Protection Agency (EPA) and U.S. Food and Drug Administration (FDA), however, have chosen not to regulate BPA due to insufficient scientific evidence of adverse human health effects at low-levels of exposure.[3,4] The National Sanitation Foundation (NSF) recommends a BPA drinking water criterion of 0.1 mg/L total allowable concentration and 0.01 mg/L single-product allowable concentration.[19] BADGE is not regulated by the EPA or FDA but the NSF recommends a drinking water criterion of 1 mg/L total allowable concentration and 5 mg/L short term exposure level.[19] While there are no regulated limits in the United States for BADGE, the European Union has established a 9 mg/kg food migration limit for BADGE and its hydrolysis products.[20]

Bisphenols in drinking water distribution systems are exposed to chemical oxidants (disinfectants) that have the potential to create degradates or by-products with more or less toxicity than the parent compounds. Two of the most common drinking water oxidants, free chorine (Cl_2/HOCl/OCl^-) and monochloramine (MCA or NH_2Cl), can each be used in the treatment plant and/or in the distribution system. Chlorination of BPA has been shown to form mono-, di-, tri- and tetra-chlorinated by-products (denoted as BPA-Cl, BPA-2Cl, BPA-3Cl, BPA-4Cl), as well as trichlorophenol (TCP).[21] The chlorinated BPAs have been detected in drinking water[22] and in epoxy-coated drinking water pipes[9]. Due to its structural similarity, BPF would be expected to follow a chlorination pathway similar to that of BPA (Figure 5.1). There are known chlorinated by-products of BADGE (BADGE-HCl, BADGE-2HCl)[23] and one of its hydrolysis products (BADGE-HCl-H2O)[24].

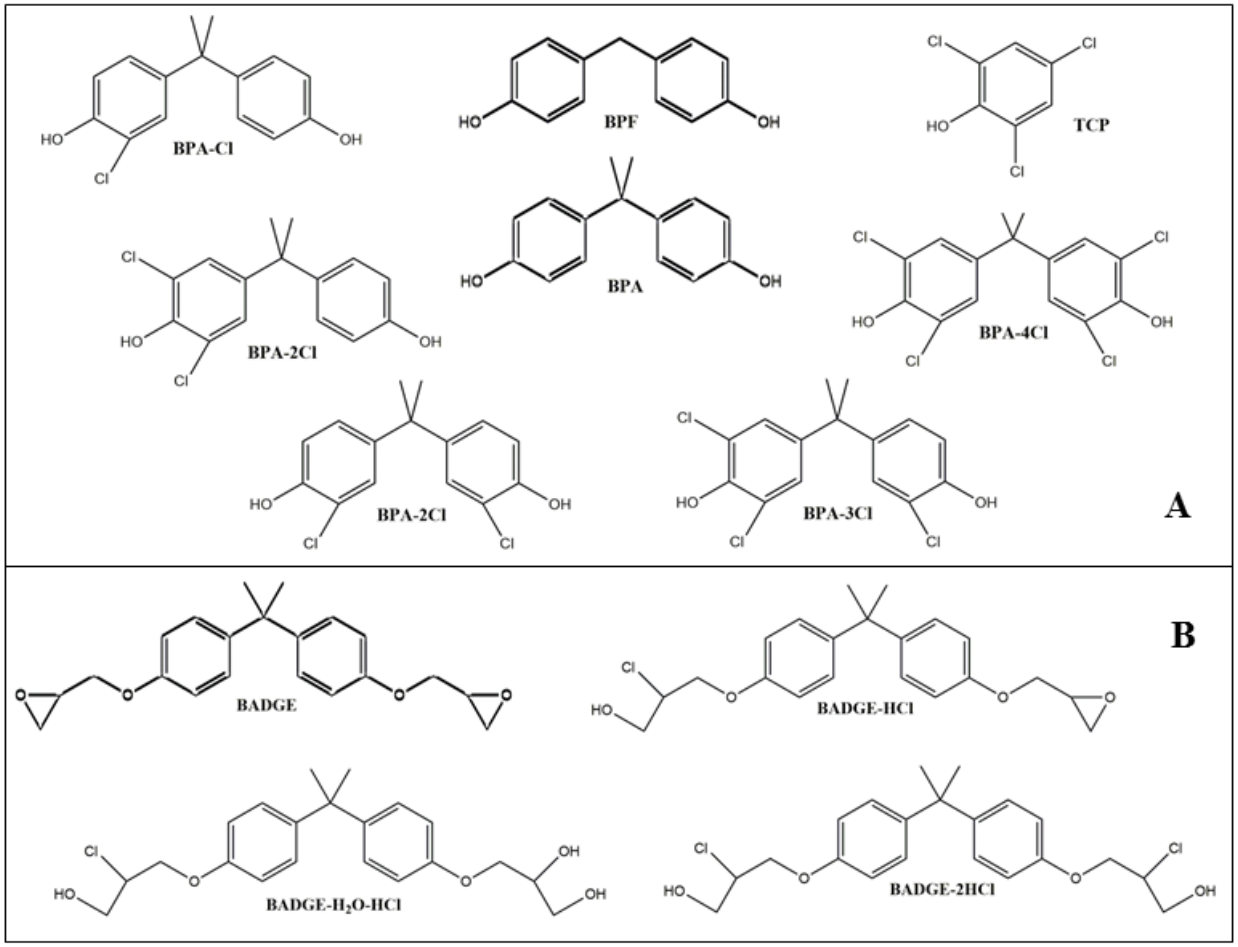

Figure 5.1 Chemical structures of key analytes: A) Structures of bisphenol A (BPA), bisphenol F (BPF), and chlorinated bisphenol A by-products; B) Epoxy prepolymer bisphenol A diglycidyl ether (BADGE) and three chlorinated BADGE by-products.

There are currently no regulatory guidelines in the United States for chlorinated bisphenols or bisphenol diglycidyl ethers but the European Union has established a 1 mg/kg food migration limit for the chlorinated BADGE by-products[20]. Because toxicity can change with chlorination there could be concerns about human exposure to chlorinated by-products of BPA and BADGE through drinking water consumption. Consumption has resulted in detectable levels of chlorinated BPA by-products in human tissue, urine, and colostrum.[25] Studies suggest that BPA by-products could be more cytotoxic, and that BPA-Cl and BPA-2Cl have a higher human α-estrogen receptor affinity (greater estrogenic activity).[26]

To estimate the concentrations and potential for human exposure through drinking water, it is necessary to understand the reaction kinetics of BPA, BPF, and BADGE. In previous work, Hu *et al.*[21] and Deborde and von Gunten[27] explored the mechanisms of BPA chlorination and Gallard *et al*.[28] studied the pseudo-first-order reaction kinetics at 20 °C. No kinetic modeling has been reported of BPA at other temperatures, of BPF or BADGE with free chlorine in general, nor of MCA reactions with any of the analytes. The purpose of this study was to explore the reactions and kinetics of both free chlorine and MCA with bisphenols (BPA and BPF) and BADGE to facilitate estimation of their concentrations over time after being leached from epoxies.

5.2 Materials and Methods

5.2.1 Reagents and Chemicals

Reagent water was prepared using a Millipore Elix Reverse Osmosis system followed by a Millipore A10 unit. Ascorbic acid, ammonium chloride, hydrochloric acid, LC/MS grade methanol (Optima), monobasic and dibasic sodium phosphate, sodium bisulfite, sodium

hydroxide and a laboratory-grade sodium hypochlorite solution were purchased from Fisher Scientific (Pittsburgh, PA). Ammonium formate, formic acid, and trichlorophenol were purchased from Sigma Aldrich (St. Louis, MO). Bisphenol A (BPA) and BPA-4Cl were purchased from TCI America (Portland, OR) and bisphenol F (BPF) from Sigma Aldrich (St. Louis, MO). Other chlorinated bisphenol A standards (BPA-Cl, BPA-2Cl, BPA-3Cl) were purchased from Santa Cruz Biotechnology (Dallas, TX). The diglycidyl ether compounds (BADGE, BADGE-H2O, BADGE-2H2O, BADGE-H2O-HCl, BADGE-HCl, BADGE-2HCl) were purchased from Sigma Aldrich (St. Louis, MO). The bisphenol internal standard, BPA-D8, was obtained from Cambridge Isotopes Laboratory (Tewksbury, MA) and the bisphenol diglycidyl ether internal standard, sulfamethoxazole-D4 (SMXL-D4), from Toronto Research Company (Toronto, Ontario, Canada). Chemical structures of the bisphenols, BADGE, and chlorinated by-products are shown in Figure 6.1. Hach Accuvac vials, monochloramine reagents, and free ammonia reagents were purchased from the Hach Company (Loveland, CO).

5.2.2 Analytical Methods

Previously described methods[29,30] were adapted for the liquid chromatography – tandem mass spectrometry (LC/MS/MS) analysis of bisphenols and diglycidyl ethers. A Shimadzu (Columbia, MD) Prominence High Performance LC (HPLC) equipped with a LC-20AB binary pump, DGU-20A3 degasser, and SIL-20A autosampler, was coupled to a 4000 Q-Trap triple-quadrupole linear ion-trap mass spectrometer with a turbo electro-spray source (AB SciEx, Framingham, MA). A reverse phase Gemini-NX C18-with-TMS-endcapping column, 150 × 3.0 mm, 3-micron particle size (Phenomenex, Torrance, CA) was used at a flow rate of 0.4 mL/min for chromatographic LC separation; and the specifications of the mobile phase were

described in a prior publication[24] The MS/MS parameters were optimized for each analyte (Table 5.1) and nitrogen gas was used for nebulization. BPA-D8 was selected as the bisphenol internal standard and SMXL-D4 for the bisphenol diglycidyl ethers. Method detection limits (MDL) were determined per Standard Methods (Method 1030C, Method Detection Limit[31]). Due to poor chromatographic response, trichlorophenol was not quantitated but was examined qualitatively during experiments.

5.2.3 Kinetic Studies

A pseudo-first-order kinetic approach was used to describe the degradation kinetics of BPA, BPF and BADGE with free chlorine and MCA. In this approach, the oxidant was present in significant excess such that its concentration was nearly constant (e.g., decreasing no more than 36% for free chlorine and 37% for MCA after 32 days) while the target species (i.e., BPA, BPF or BADGE) degraded. BPA or BPF was spiked at a nominal concentration of 200 μg/L into a 2 mg/L (as Cl_2) chlorine solution buffered with 5 mM phosphate to a pH of from 2 to 12. This buffer concentration was chosen to control pH effectively in solutions with activity corrections of less than one percent (which could then be neglected in the kinetic and equilibrium modeling). Temperatures were held constant throughout the bisphenol experiments at either 10 or 25 °C. BADGE was spiked at a nominal concentration of 200 μg/L into a 2 mg/L (as Cl_2) chlorine solution buffered with 5 mM sodium phosphate to a pH of from 7 to 9, and maintained at a constant 25 °C throughout. Samples were collected at predetermined times for LC/MS/MS analysis of the parent bisphenols and selected chlorination by-products (Figure 5.1). Sodium bisulfite was used to quench chlorine immediately after sampling. Initial and final free chlorine concentrations were determined using the Hach Total Chlorine Method 8167 (an EPA-approved

Table 5.1 LC/MS/MS method parameters and method detection limits (MDL) for bisphenols, bisphenol diglycidyl ethers, and internal standards.

Compound	CAS Number	MS Ionization Mode	Quantitation or Confirmation	Ion	Precursor Ion, m/z	Product Ion, m/z	Declustering Potential (V)	Collision Energy (V)	Collision Cell Exit Potential (V)	MDL (µg/L)
BPA	**80-05-7**	**negative**	**Quant**	**$[M-H]^-$**	**227.0**	**212.0**	**-76.02**	**-24.87**	**-3.12**	**0.057**
			Conf	$[M-H]^-$	227.0	133.0	-76.02	-31.26	-10.35	
BPA-Cl	**74192-35-1**	**negative**	**Quant**	**$[M-H]^-$**	**261.7**	**181.9**	**-69.59**	**-41.39**	**-12.97**	**13.6**
			Conf	$[M-H]^-$	261.7	245.8	-44.96	-29.12	-14.74	
BPA-2Cl	**79-98-1**	**negative**	**Quant**	**$[M-H]^-$**	**295.0**	**243.8**	**-84.88**	**-32.91**	**-5.10**	**1.8**
			Conf	$[M-H]^-$	295.0	216.1	-49.95	-41.35	-32.37	
BPA-3Cl	**40346-55-2**	**negative**	**Quant**	**$[M-H]^-$**	**330.6**	**252.0**	**-40.15**	**-44.21**	**-8.36**	**3.2**
			Conf	$[M-H]^-$	330.6	278.0	-52.96	-35.24	-12.26	
BPA-4Cl	**79-95-8**	**negative**	**Quant**	**$[M-H]^-$**	**365.0**	**314.0**	**-81.19**	**-35.77**	**-13.06**	**5.9**
			Conf	$[M-H]^-$	365.0	286.0	-33.04	-45.66	-13.26	
TCP	**88-06-2**	**negative**	**Quant**	**$[M-H]^-$**	**194.7**	**35.0**	**-29.98**	**-44.79**	**-3.50**	**NC**
			Conf	$[M-H]^-$	194.7	158.8	-64.45	-29.97	-24.66	
BPF	**620-92-8**	**negative**	**Quant**	**$[M-H]^-$**	**199.0**	**93.0**	**-67.19**	**-29.07**	**-6.88**	**0.18**
			Conf	$[M-H]^-$	199.0	105.0	-70.68	-28.42	-5.56	
BPA-D8	**92739-58-7**	**negative**	**Quant**	**$[M-H]^-$**	**235.0**	**220.0**	**-76.20**	**-25.68**	**-4.58**	**NA**
			Conf	$[M-H]^-$	235.0	137.0	-78.04	-35.62	-8.86	
BADGE	**1675-54-3**	**positive**	**Quant**	**$[M+NH_4]^+$**	**358.2**	**191.0**	**51.95**	**21.49**	**12.04**	**7.0**
			Conf	$[M+NH_4]^+$	358.2	135.0	51.95	43.41	7.61	
BADGE-HCl	**13836-48-1**	**positive**	**Quant**	**$[M+NH_4]^+$**	**394.0**	**227.0**	**42.89**	**19.78**	**14.17**	**0.48**
			Conf	$[M+NH_4]^+$	394.0	135.0	42.89	45.21	6.71	
BADGE-H2O-HCl	**227947-06-0**	**positive**	**Quant**	**$[M+NH_4]^+$**	**412.8**	**135.0**	**38.50**	**48.57**	**6.11**	**7.6**
			Conf	$[M+NH_4]^+$	412.8	227.1	38.50	21.93	13.80	
BADGE-2HCl	**4809-35-2**	**positive**	**Quant**	**$[M+NH_4]^+$**	**431.3**	**229.0**	**51.65**	**22.45**	**15.11**	**2.9**
			Conf	$[M+NH_4]^+$	431.1	227.0	54.59	23.48	13.81	
SMXL-D4	**1020719-86-1**	**positive**	**Quant**	**$[M+H]^+$**	**258.0**	**96.0**	**56.36**	**45.25**	**17.08**	**NA**
			Conf	$[M+H]^+$	258.0	112.0	72.14	35.41	5.62	

NC = Not calculated - Poor chromatography so peak was used qualitatively *NA = Not applicable*

method based on the USEPA DPD Method[32]) with a Hach DR 5000 UV-Vis Spectrophotometer (Loveland, CO). The chloramination experiments were conducted in the same manner as the free chlorination experiments. For the chloramination experiments, MCA was prepared by spiking hypochlorous acid into an ammonium chloride solution at pH 8.9 resulting in a MCA concentration of 3.5 to 4 mg/L as Cl_2 determined using the Hach Chloramine (Mono) Indophenol Method 10200[33]. The monochloramine was prepared such that a 0.1 mg/L as N excess of ammonium was present (verified using the Hach Nitrogen, Free, Ammonia Indophenol Method 10200[33]).

5.3 Results and Discussion

5.3.1 The Chlorination Model

BPA and BPF have two acidic (phenolic) functional groups. The dissociation of BPA is described by:

$$BPA \leftrightarrow BPA^- + H^+ \ (pK_{a1,BPA} = 10.05\ (10\ °C),\ 9.78\ (25\ °C)) \qquad (1)$$

$$BPA^- \leftrightarrow BPA^{2-} + H^+ \ (pK_{a2,BPA} = 10.81\ (10\ °C),\ 10.53\ (25\ °C)) \qquad (2)$$

The pK_{a1} and pK_{a2} values for BPF were calculated to be the same as for BPA (Hilal et al.[34]; SPARC Release v.4.6). The free chlorine HOCl/OCl^- couple has a $pK_{a,HOCl}$ of 7.69 at 10 °C and 7.54 at 25 °C.[35] Thus, for the reaction of a bisphenol and free chlorine, there are three bisphenol species and two chlorine species potentially involved, such that at least six different reactions may occur simultaneously albeit at varying rates.

The total BPA concentration can be described as:

$$[BPA]_T = [BPA]+[BPA^-]+[BPA^{2-}] \qquad (3)$$

and the total free chlorine concentration as:

$$[HOCl]_T = [HOCl] + [OCl^-] \quad (4)$$

The rate of reaction of BPA with free chlorine is, hence:

$$-d[BPA]/dt = k_{eff} \cdot [HOCl]_T \cdot [BPA]_T = (k_{eff} \cdot [HOCl]_T) \cdot [BPA]_T = k' \cdot [BPA]_T \quad (5)$$

where k_{eff} is the apparent second-order rate constant. Because the free chlorine concentration was in significant excess, and its concentration was nearly constant throughout the experiment, the free chlorine concentration can be combined with k_{eff} to form the pseudo-first-order rate constant (k'). This constant (k') can be experimentally determined by acquiring concentrations of BPA (or BPF) versus time, and regressing the data as:

$$-\ln(BPA/BPA_0) = k' \cdot t \quad (6)$$

where k' is the slope determined by least squares linear regression. Once k' is determined, the second-order k_{eff} can be determined as:

$$k_{eff} = k'/[HOCl]_T \quad (7)$$

In addition to the six aforementioned reactions, Gallard *et al*.[28] also showed that an acid-catalyzed reaction also takes place between BPA and HOCl, that is:

$$BPA + HOCl + H^+ \leftrightarrow \text{products} \ (k_1) \quad (8)$$

To simplify, it is assumed that the reactivity of HOCl with each BPA species is many times that of OCl^- (as is true for many chlorination reactions) such that the reactions of OCl^- were assumed negligible.[28] This leaves three primary reactions (in addition to the acid-catalyzed reaction) as:

$$BPA + HOCl \leftrightarrow \text{products} \ (k_2) \quad (9)$$

$$BPA^- + HOCl \leftrightarrow \text{products} \ (k_3) \quad (10)$$

$$BPA^{2-} + HOCl \leftrightarrow \text{products} \ (k_4) \quad (11)$$

The overall reaction of BPA and free chlorine is, therefore, described by:

$$-d[BPA]_T / dt = [HOCl] \cdot (k_1 \cdot [BPA] \cdot [H^+] + k_2 \cdot [BPA] + k_3 \cdot [BPA^-] + k_4 \cdot [BPA^{2-}])$$

$$= [HOCl]_T \cdot [BPA]_T \cdot (\alpha_{HOCl} \cdot (k_1 \cdot \alpha_1 \cdot [H^+] + k_2 \cdot \alpha_2 + k_3 \cdot \alpha_3 + k_4 \cdot \alpha_4))$$

$$= [HOCl]_T \cdot [BPA]_T \cdot k_{eff} \qquad (12)$$

where α_1, α_2, α_3 and α_4 are the ionization fractions of BPA in the acid catalyzed, neutral, mono-anionic and di-anionic forms at a given pH, respectively. Substituting in for each ionization fraction gives:

$$k_{eff} = \frac{k_1 \cdot [H^+]^4 + k_2 \cdot [H^+]^3 + k_3 \cdot K_{BPA1} \cdot [H^+]^2 + k_4 \cdot K_{BPA1} \cdot K_{BPA2} \cdot [H^+]}{[H^+]^3 + (K_{BPA1} \cdot K_{a,HOCl}) \cdot [H^+]^2 + (K_{BPA1} \cdot K_{a,HOCl} + K_{BPA1} \cdot K_{BPA2}) \cdot [H^+] + K_{BPA1} \cdot K_{BPA2} \cdot K_{a,HOCl}} \qquad (13)$$

where $[H^+] = 10^{-pH}$, $K_{BPA1} = 10^{-pK,a1,BPA}$, $K_{BPA2} = 10^{-pK,a2,BPA}$, and $K_{a,HOCl} = 10^{-pK,HOCl}$.

The experimental procedure was to conduct oxidation experiments at varied pH (at constant temperature), determine k' (the pseudo-first-order rate constant) using linear regression, and to calculate k_{eff} as a function of pH. Next, a least-squares non-linear regression method was used to minimize the difference between experimental ($k_{eff,exp}$) and modeled ($k_{eff,model}$) rate constants by adjusting the individual kinetic rate constants (i.e., k_1, k_2, k_3 and k_4).

5.3.2 Chlorination of Bisphenols

The free chlorination kinetic rate constants, k_1 through k_4, are tabulated in Table 5.2 for both BPA and BPF for the data generated in this study at 10 °C and 25 °C. Constants generated by Gallard et al.[28] at 20 °C are also tabulated in Table 5.2. Differences in the values obtained by Gallard et al.[28] and in this study may be due to several causes. The BPA dissociation constants, pK_1 and pK_2, used in this study were 9.87 and 10.62, respectively, at 20 °C (as determined using SPARC v.4.6; Hilal et al.[34]) whereas values of 9.60 and 10.20 were used by Gallard et al.[28] (based

on work by Kosky et al.[36]). These relatively minor differences in pK values have a large effect on the constants derived from the model described in Equation 13. Additionally, this study was designed to focus on varied oxidants (i.e., free chlorine and MCA), temperatures, and reactants (i.e., BPA, BPF, and BADGE), while Gallard et al.[28] focused on developing the model using only BPA with free chlorine at 20 °C and many more pH values. For the most critical individual constants for drinking water (e.g., k_3 and k_4 for the reactions with the BPA^- and BPA^{2-}, respectively), Gallard et al.[28] determined constants that were approximately 2 and 4 times lower, respectively, than those determined in this study. The effective chlorination rate constant was lower for the reaction with BPF as compared with BPA (Figures 5.2 and 5.3).

Half-lives were calculated as a function of pH for an assumed free chlorine concentration of 1 mg/L as Cl_2 (Figure 5.4). Half-lives ranged from 3 min to 35 min over the pH range from 6 to 11, for BPA and BPF at 10 °C and 25 °C. These results show that BPA has a shorter half-life than BPF over a wide pH range. Half-lives were lower at higher temperature, consistent with kinetic theory. Due to the nature of speciation of both free chlorine and the bisphenols, half-lives were lowest over the pH range from 8 to 10. Thus, BPA and BPF can both be presumed to degrade rapidly in systems with free chlorine present.

5.3.3 Oxidation By-products Formed During Chlorination of BPA

The formation of mono-, di-, tri- and tetra-chloro-BPA was tracked in the oxidation experiments using LC/MS/MS. The data show that appreciable conversion of BPA to its chlorinated oxidation by-products occurred with short exposure times at the nominal free chlorine concentration of 2 mg/L (as Cl_2) used in the experiments (Figure 5.5; Appendix Figures A.4.2.1 and A.4.2.2). At higher temperature (25°C vs. 10°C), the removal of BPA was more rapid

Table 5.2 Rate constants and dissociation constants for BPA and BPF oxidation by free chlorine.

	BPA			BPF	
Constants	**10 °C (this study)**	**25 °C (this study)**	**20 °C (Gallard)***	**10 °C (this study)**	**25 °C (this study)**
k_1	8.9E+05	2.0E+06	3.8E+04	4.2E+05	7.6E+05
k_2	1.9E+01	2.1E+01	1.8E+00	2.0E+01	2.0E+01
k_3	5.9E+04	6.0E+04	3.1E+04	3.9E+04	4.0E+04
k_4	2.0E+05	2.7E+05	6.6E+04	2.3E+05	2.4E+05
pK_{aHOCl}	7.69	7.54	7.54	7.69	7.54
pK_{a1BP}	10.05	9.78	9.60	10.05	9.78
pK_{a2BP}	10.81	10.53	10.20	10.81	10.53

*Gallard *et. al.*[28]

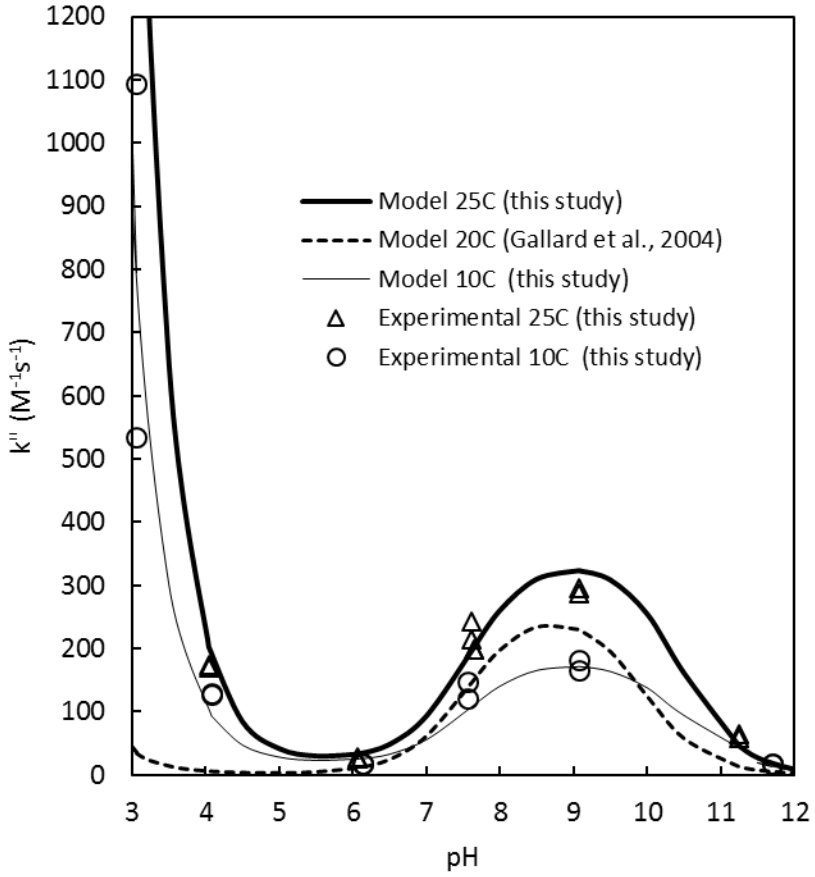

Figure 5.2 Experimental, modeled, and previously published second-order rate constants ($M^{-1}s^{-1}$) for BPA with free chlorine ($HOCl/OCl^-$).

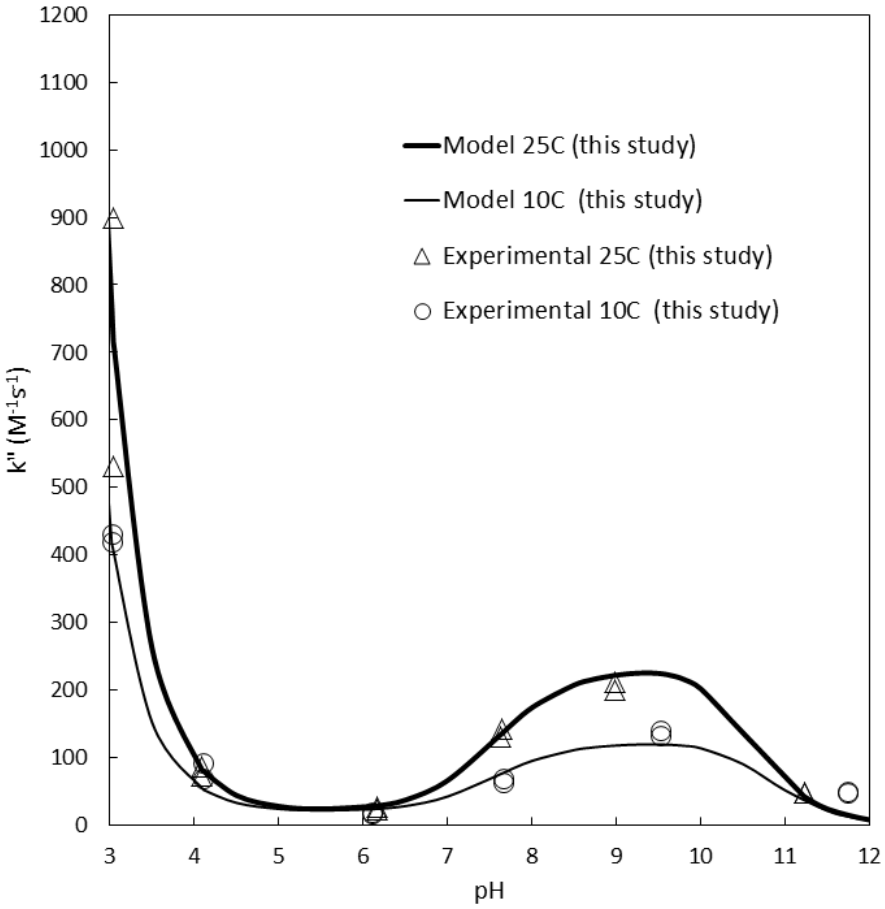

Figure 5.3 Experimental and modeled second-order rate constants ($M^{-1}s^{-1}$) for BPF with free chlorine ($HOCl/OCl^-$).

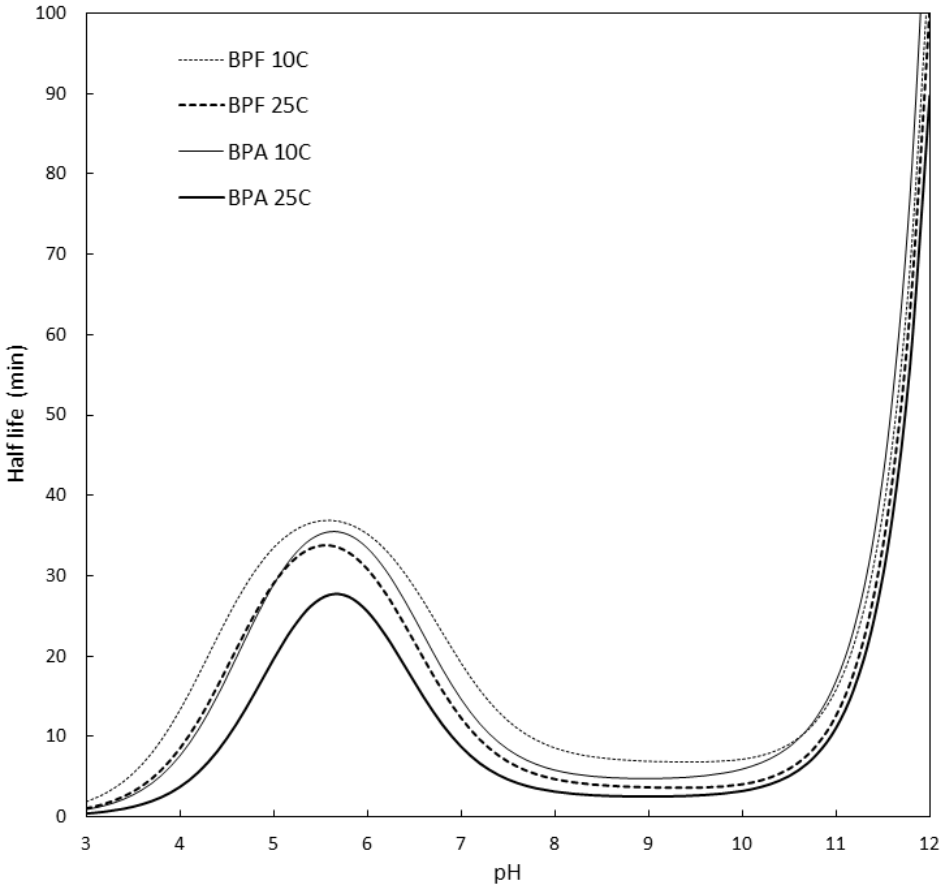

Figure 5.4 Half-lives (min) for BPA and BPF as a function of pH when exposed to 1 mg/L Cl_2 at 10 °C and 25 °C.

and by-products were formed more quickly. Thus, a greater percentage of the overall mass balance was attributable to by-products than the parent (BPA) at 25°C than at 10°C (Figure 5.5). The overall mass balance (i.e., the sum of the by-products and BPA) was also lower at 25°C than at 10°C due to faster kinetics driving reactions toward other (unmonitored) by-products. The chlorination process can be complicated and has the potential to form additional chlorinated by-products which can include ring cleavage and reactions with and among the chlorinated by-products.[21,37] With respect to pH effects, BPA was observed to degrade faster at pH 9.1 than at 7.6 (Figure 5.5). However, the overall mass balance (i.e., the sum of BPA plus the four chloro-by-products) was observed to be greater at pH 9.1 than at 7.6 showing that other by-products are more favored at pH 7.6 than at 9.1. At this chlorine concentration, half-lives were less than five minutes at both pH values (7.6 and 9.1) and both temperatures (10 and 25 °C).

5.3.4 Monochloramination of Bisphenols

BPA and BPF were both relatively stable in the presence of MCA, with half-lives from approximately 0.75 to 9 days at a nominal MCA concentration of 3.5 mg/L as Cl_2 (Figure 5.6; Appendix Figures A.4.2.3 and A.4.2.4). BPA was more stable at higher pH (approximately 8.9 vs. 7.6) and at lower temperature (10 °C vs. 25 °C). BPF was also more stable at a lower temperature, but its stability varied little with pH at either temperature (Appendix Table A.4.1.1). These experiments were limited to a pH range of 7 to 9 to ensure the form of chlorine was mainly MCA (avoiding formation of dichloramine and trichloramine). The results indicate that BPA and BPF can be expected to degrade slowly via MCA oxidation over relevant time frames in drinking water distribution systems using (Figure 6.6 for BPA). As with free chlorine, the sum of the by-products again was rapidly reduced during monochloramination, evidence

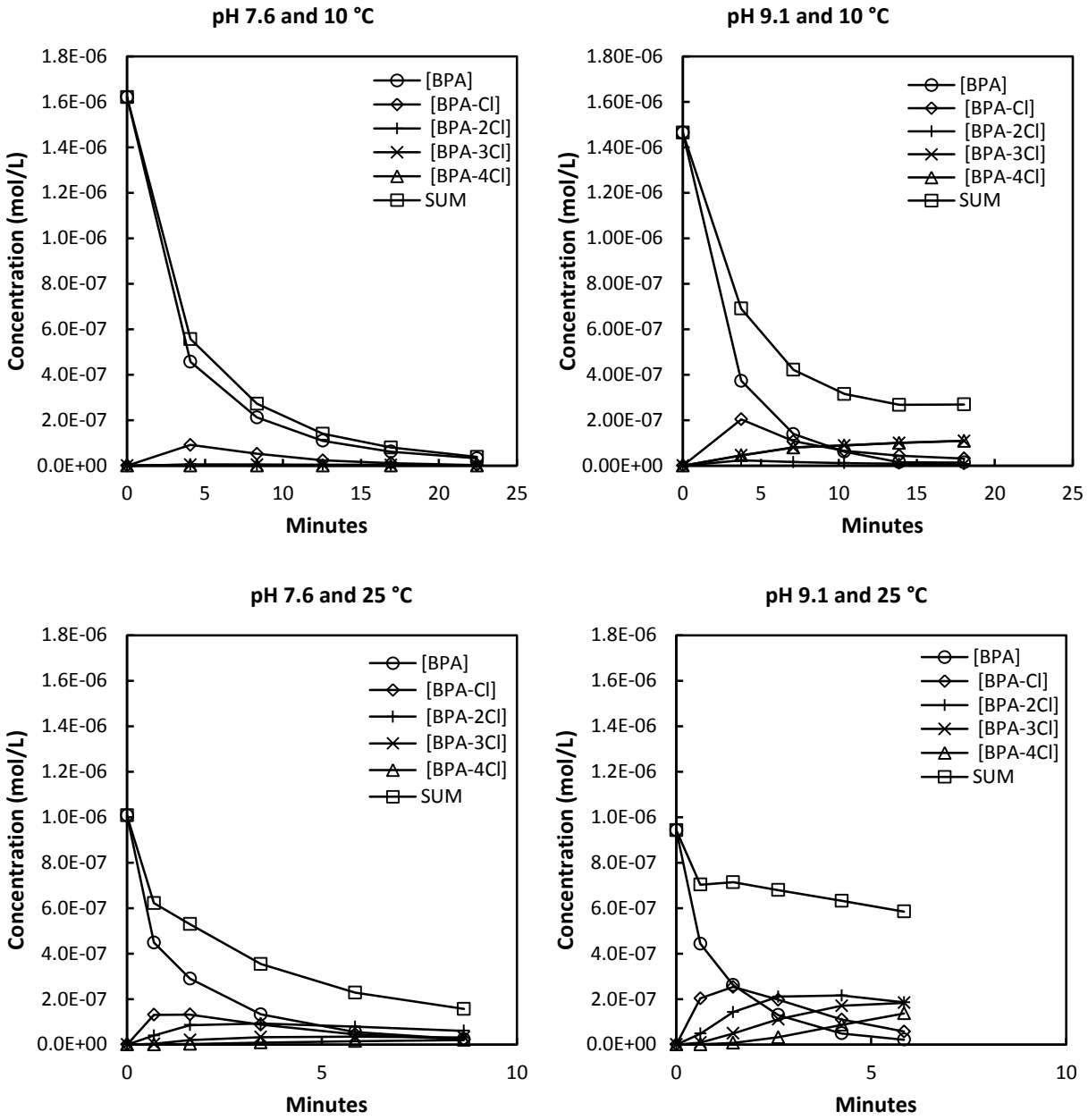

Figure 5.5 BPA decay and the formation of chlorinated by-products during the oxidation of BPA with free chlorine ($HOCl/OCl^-$) at pH 7.6 and 9.1 with temperatures of 10 °C and 25 °C. Free chlorine concentration averaged 2.1 mg/L (as Cl_2) at pH 7.6 and 2.4 mg/L (as Cl_2) at pH 9.1. All experiments were run in duplicate with averaged values shown; each replicate plot is shown in Appendix Figures A.4.2.1 and A.4.2.2.

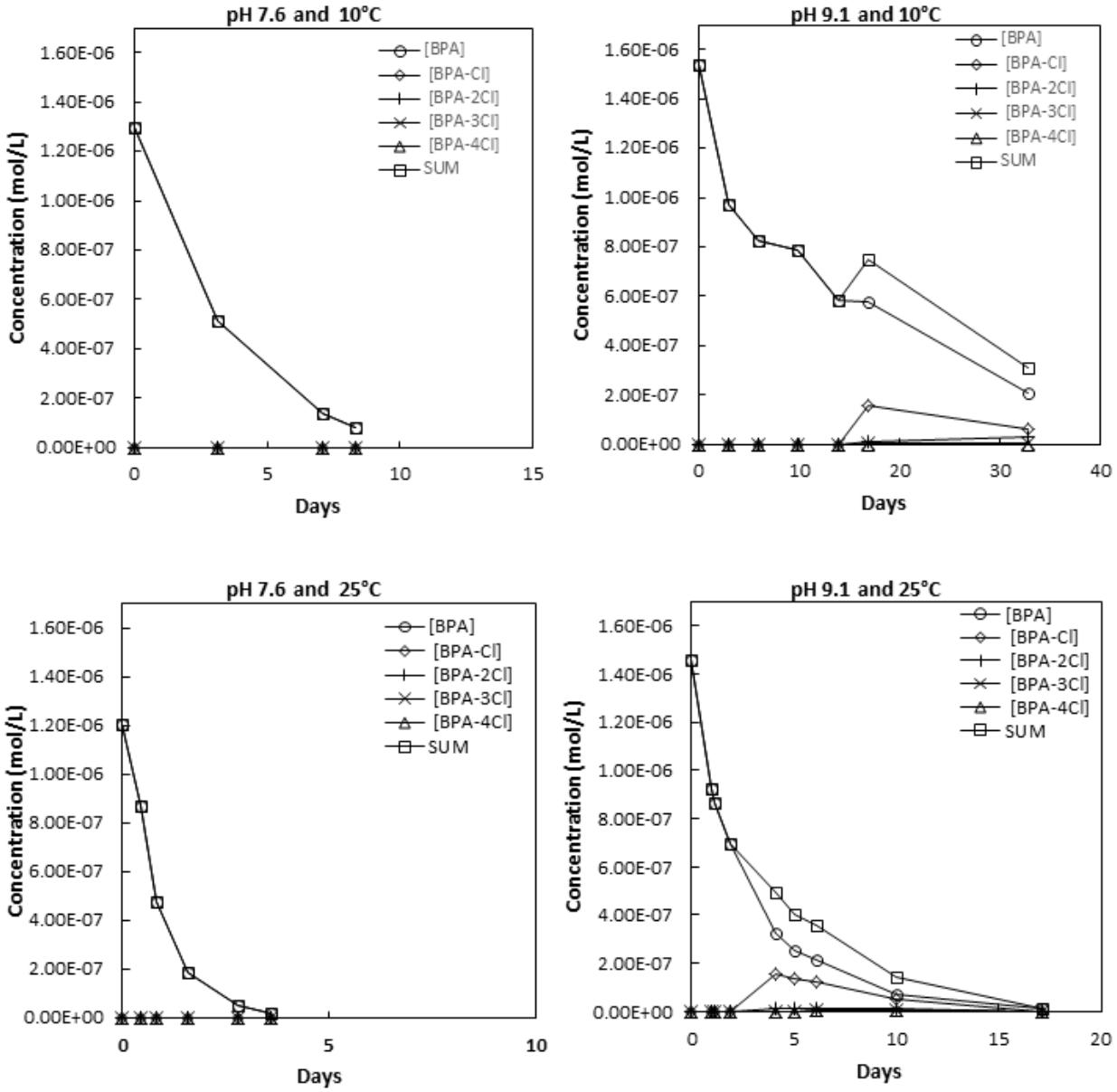

Figure 5.6 BPA decay and the formation of chlorinated by-products during the oxidation of BPA with monochloramine (NH_2Cl) at pH 7.6 and 9.1 with temperatures of 10 °C and 25 °C. Monochloramine concentration averaged 3.7 mg/L (as Cl_2) at pH 7.6 and 3.7 mg/L (as Cl_2) at pH 9.1. All experiments were run in duplicate with averaged values shown; each replicate plot is shown in Appendix Figures A.4.2.3 and A.4.2.4.

that by-products other than the mono-, di-, tri- and tetra-chloro-BPAs were being formed (Figure 6.6). The MCA reaction pathways with organic chemicals differ from those of free chlorine[38] and the chlorine intermediate species or by-products being formed could be different from those formed with free chlorine.

5.3.5 Chlorination and Monochloramination of BADGE

While degradation of BADGE was observed in the presence of either free chlorine or MCA, at pH values ranging from 7.6 to 9.1, the rate of degradation was consistent with the hydrolysis rate of BADGE as determined in a separate set of experiments and modeled as a function of pH and temperature.[24] That is, the reactivity of BADGE was not enhanced at all over its hydrolysis rate by either free chlorine or MCA. Chlorinated by-products of BADGE (BADGE-HCl, BADGE-2HCl, and BADGE-H_2O-HCl) were not detected during any of the chlorination experiments. The hydrolysis rate of BADGE results in half-lives on the order of from 11 to 4.5 days at 15 °C and 25 °C across the pH range of 5 to 9.[24]

The propensity for chlorine to oxidize bisphenols (BPA and BPF) but not BADGE is explained by differences in chlorination chemistry. Chlorination of the phenol rings in BPA and BPF occurs through a chlorine substitution reaction and subsequent dehydration.[21] The location of the chlorine substitution on the phenol rings is directed by the activating hydroxyl groups which directs the chlorine to activated ortho positions because the para positions are already occupied and the meta positions are not activated.[39]

Potential sites for chlorination of BADGE are on the phenol ring or on the side chain epoxide groups. The BADGE phenol rings have a less activating ether group and, therefore, do not have strongly activated ortho positions. The first step in epoxide chlorination

is a ring-opening step that is common under acidic or basic conditions. Acidic conditions protonate the epoxide to form a strong electrophile, while in alkaline conditions a strong base attacks and opens the ring forming an alkoxide.[40] After ring opening, the second step is the addition of chlorine through an S_N2 mechanism.[40] Under drinking water conditions, the pH is near neutral and does not faciliate the initial ring opening step, effectively preventing chlorination of the epoxides.

5.4 Conclusions

The bisphenols BPA and BPF, along with BADGE, have the potential to be present in drinking water distribution systems, where they can be exposed to free or combined chlorine. Exposure to free chlorine can cause the rapid degradation of the bisphenols, with half-lives ranging from less than one minute to 35 min under typical conditions, resulting in the formation of chlorinated degradation products with greater or lesser toxicity. The bisphenols are much more stable, however, when exposed to MCA, a key residual disinfectant in water treatment systems. While BADGE will hydrolyze in drinking water, with estimated half-lives of approximately 5 hours to 5 days at 25 °C[24], there is no increased degradation associated with either free chlorine or monochloramine at conditions typical of drinking water treatment and distribution.

5.5 References

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Chapter 6: Summary, Conclusion, and Future Directions

6.1 Research Summary

The purpose of this research was to evaluate an epoxy coating and a polyethylene terephthalate (PET) liner for key organic leachates, i.e., compounds present in the starting materials that may leach into water or form by-products in concentrations high enough to be of public health or regulatory concern. Bisphenols and bisphenol diglycidyl ethers (BDGEs) were selected as the key epoxy leachates (Chapter 1, Section 1.3) and phthalate esters (PAEs) and phthalic acids (PAs) as the key PET leachates (Chapter 1, Section 1.2). The main objectives were to develop analytical methods for identification of the key organic leachates from an epoxy coating and PET liner and determine the hydrolysis and chlorination reactions of key leachates in drinking water. The specific aims of the analytical method development were to develop a liquid chromatography/mass spectrometry (LC/MS/MS) or GC/MS methods for the key organic leachates, eliminate potential contamination sources, and apply the analytical methods during fill-and-dump (FD) pipe studies. The specific aims for the determination of the reactions in drinking water were to investigate hydrolysis of key analytes and chlorination of key analytes with free chlorine and monochloramine; to develop a kinetic model to predict analyte concentrations after hydrolysis or chlorination; and to monitor the formation of key hydrolysis and chlorination by-products.

6.2 Research Conclusions

6.2.1 Method Development for Key Leachates and By-products (Chapter 2)

To detect organic compounds leached from the lining or coating, low-level (μg/L) analytical methods were developed for the key organic leachates and possible contaminant

sources were eliminated. LC/MS/MS methods were developed for the bisphenols (BPA, BPB, BPD, BPE, BPF), chlorinated BPA by-products (BPA-Cl, BPA-2Cl, BPA-3Cl, BPA-4Cl), BDGEs (BADGE, BFDGE), BDGE hydrolysis by-products (BADGE-H_2O, BADGE-$2H_2O$, BADGE-H_2O-HCl, BFDGE-H_2O, BFDGE-$2H_2O$, BFDGE-H_2O-HCl), BDGE chlorination by-products (BADGE-HCl, BADGE-2HCl, BADGE-H_2O-HCl, BFDGE-HCl, BFDGE-2HCl, BFDGE-H_2O-HCl) and PAs (PA, IPA, TPA). Syringe filtration was used prior to bisphenol analysis to prevent clogging of the LC system and column from debris of unlined or uncoated pipe sections. Mixed cellulose ester (MCE), nylon, polytetrafluoroethylene, and polycarbonate filter membranes were investigated and MCE was selected since it did not leach or adsorb statistically significant amounts of the bisphenols. Frequent instrumental and procedural blanks, high purity solvents, and solvent rinsing of glassware were sufficient to reduce background contaminant levels. A GC/MS method with liquid-liquid extraction was developed for the PAEs (DMP, DMTP, DMIP, DEP, DETP, DNBP, BBP, DEHA, DEHP, DNOP). LC/MS was not used for PAE analysis because significant instrumental background levels could not be eliminated. Method detection limits (MDLs) were 0.057 to 14 µg/L for the bisphenols, 0.24 to 7 µg/L for the BDGEs, 0.53 to 4 µg/L for the PAs, and ≤1 to 10 µg/L for the PAEs. These MDLs were low enough to provide leachate data relevant to regulatory or recommended levels (Chapter 1, Sections 1.2.2 and 1.3.2).

6.2.2 Fill-and-Dump Sampling of Epoxy-Coated and PET-Lined Pipe Sections (Chapter 2)

The fill-and-dump (FD) experiments determined the concentrations of key leachates from an epoxy coating and a PET liner using the developed analytical methods. The FD pipe setup maximized the potential for detecting organic chemicals leaching into drinking water because it combined a high ratio of surface area to volume with long holding times,

representing a worst-case scenario for the concentrations of epoxy or PET leachates in drinking water to which a consumer might be exposed.

Materials in contact with the FD samples (e.g., sample bottles, lids, pipets, pipe nipples) were tested and found to not leach or adsorb statistically significant concentrations of the key leachates, with two exceptions. Significant adsorption of BADGE on silicone stoppers was observed after 6 hours and at longer contact times; silicone stoppers were used during the fill-and-dump experiments on epoxy-coated pipe sections, so the concentrations of BADGE and its hydrolysis products observed in those experiments (FD1 and FD2) are likely under-reported. High-density polyethylene (HDPE) stoppers were used with the PET-lined pipe sections, from which samples were drawn for analysis of PAEs and PAs. HDPE stoppers exhibited little or no adsorption of PAs and 7 PAEs, but significantly adsorbed three PAEs (BBP, DEHA, and DNBP) after 7 days (but not after 18 hours).

The starting components of the epoxy coating were analyzed and the resin component was found to contain BADGE. Extraction waters from epoxy-coated pipe sections were analyzed shortly after coating (FD1), and BADGE, BPA, and compounds that mimicked BPA (BPA-like) were detected. BADGE was detected in 9 of the 36 samples and ranged from 13 to 340 µg/L; high concentrations were associated with 6 to 24 hour holding times, and the combination of BADGE hydrolysis and adsorption of BADGE on the silicone stoppers appears to be responsible for the lack of BADGE detection at longer holding times. BPA was detected in 5 of the 36 samples and ranged from 0.25 to 1.7 µg/L. BPA-like compounds were detected in 31 of the 36 samples and ranged from 0.94 to 94 µg/L.

The epoxy-coated pipe sections were stored for 7 months and then a second fill-and-dump experiment (FD2) was performed. BPA, BPA-like compounds, BADGE-H_2O, BADGE-H_2O-like compound, and BADGE-$2H_2O$ were detected. BPA was detected in 35 of the 38 samples and ranged from 0.22 to 12 µg/L. BPA-like compounds were detected in all 38 samples and ranged from 0.17 to 194 µg/L. BADGE-H_2O was detected in 2 of the 38 samples and ranged from 3.2 to 4.6 µg/L. The BADGE-H_2O-like compound was detected in 32 of the 38 samples and ranged from 1.1 to 98 µg/L (assuming a response equivalent to BADGE-H_2O). BADGE-$2H_2O$ was detected in 23 of the 38 samples and ranged from 0.83 to 91 µg/L. BADGE was not detected in FD2 and the other bisphenols (BPB, BPD, BPE, BPF, BPS, BPA-4Cl) were not observed during FD1 or FD2. Leached BPA and BADGE concentrations did not significantly exceed drinking water recommendations from the National Sanitation Foundation (0.1 mg/L total allowable BPA concentration, 5 mg/L short term BPA exposure level, and 1 mg/L total allowable BADGE concentration), nor did BPA exceed the Environmental Protection Agency's BPA daily intake limit of 0.05 mg/kg-bw/day (mg per kg of body weight per day) assuming a body weight of 23 to 136 kg (50 to 300 lb) and 2 to 3.7 L daily water intake.

Leaching of PAs and PAEs was not observed from the PET lined pipe sections (FD3) or in subsequent exposure of PET liner to organic solvents. The lack of leaching is attributed to the purity of the PET liner and curing process. Unlike the epoxy coating, the PET is cured prior to insertion into the pipe section and does not cure in place.

A chlorine demand was observed when the epoxy coated pipe specimens were filled with chlorinated pH 8 extraction water; 73 to 99% of the starting chlorine concentration was consumed. Interaction with chlorine could prematurely age a lining or coating and can

influence chlorine residuals at the tap, biological growths in the service line, and disinfection by-product formation. The chlorine demand observed with the PET liner was lower and was attributed to impurities present in the pipe or end-fittings and not a reaction with the PET itself.

6.2.3 BPA-Like Compounds (Chapters 2 and 3)

During the epoxy coating fill-and-dump experiments BPA-like compounds were observed that had different LC (reverse phase) retention times than BPA. The main BPA-like compound, eluting at 6.0 min, had the same LC/MS and GC/MS mass spectra, quantitation-to-confirmation ion ratio, and time-of-flight MS exact mass. The reverse phase LC retention times of structurally similar compounds (e.g., *m,p'*-BPA, *p,p'*-BPA-2CH_3, *o,o'*-BPF, *p,p'*-BPF-2CH_3) were investigated but none of the retention times matched the 4.4, 5.7, 5.9, 6.0, 6.3, and 7.4 min observed for the BPA-like compounds (versus 6.6 min for BPA). BADGE hydrolysis products have been reported to mimic BPA in negative mode electrospray. When a chlorinated BADGE standard was analyzed a peak was observed with a similar retention time to BPA-like compound A (the BPA-like compound with a 6.0 min retention time). The chlorinated BADGE standard was presumed to have hydrolyzed to BADGE-2H_2O. However, upon comparison of the FD2 data, there was not a strong correlation between the observed concentrations of BADGE-2H_2O and BPA-like compound A. Additional data is required to determine if any of the BPA-like compounds are BADGE hydrolysis products.

With the major difference between BPA and the BPA-like compounds being chromatographic, it was posited that complexation was occurring. All but one of these complexes would have less hydrophobicity than BPA (shorter LC retention times than BPA) and dissociate as the BPA-like compounds passed through the LC column or in the negative-mode

electrospray ionization process, yielding detection of only BPA at the altered retention times. Potential complexion agents in drinking water were investigated, including lead ($PbCl_2$), copper ($CuSO_4$), ammonium bicarbonate, calcium chloride, magnesium chloride, and ferrous ammonium sulfate), but only a common epoxy starting material, triethylenetetramine (TETA), produced a BPA-like chromatographic peak, and the peak was relatively small. The peak was similar to the smaller 4.5 to 5.9 min BPA-like compounds observed during FD2. The implication of this is that studies addressing occurrence, transformation, or fate of BPA and related compounds should also consider retention times surrounding BPA.

6.2.4 Reactivity of Key Analytes: Hydrolysis (Chapter 4)

A kinetic model was developed to predict concentrations of BADGE and BFDGE over time as a function of pH and temperature. Based on experimental data and modeling efforts, the half-lives of BADGE at pH 7 and temperatures of 15, 25, 35, and 40 °C are estimated to be 11, 4.6, 2.0, and 1.4 days respectively; and the BFDGE half-life at pH 7 and 25 °C is estimated to be 5 days. The hydrolysis rates of both BADGE and BFDGE are relatively constant at pH values of 5–10, but increase significantly at higher and lower pH values; that is, the hydrolysis of these compounds is both acid and base catalyzed. A full kinetic model was not developed for BFDGE but it hydrolyzed similarly to BADGE. Three key hydrolysis by-products (BADGE-H_2O, BADGE-$2H_2O$, BADGE-H_2O-HCl) were monitored, with BADGE-H_2O and BADGE-$2H_2O$ observed during hydrolysis. BADGE-$2H_2O$ was the final end product under the time, temperature, and pH conditions studied, which encompasses conditions representative of those encountered in drinking water distribution systems. These half-lives are on timescales relevant to drinking water service lines because measureable changes in the concentrations of BADGE, BFDGE, and

their hydrolysis by-products can potentially occur when water is left standing in the service line overnight or for longer periods of time.

BPA was not observed to hydrolyze in 30 days at pH values of 2 to 12 and temperatures of 25 and 40 °C. The bisphenol chemical structure does not promote hydrolysis reactions. Due to structural similarity with BPA, the other bisphenols (BPB, BPD, BPE, BPF, and BPS) were not investigated for hydrolysis.

6.2.5 Reactivity of Key Analytes: Chlorination (Chapters 2 and 5)

Bisphenols (BPA, BPB, BPD, BPE, BPF) are susceptible to chlorination and chloramination; chlorination was rapid (complete loss of starting bisphenol compound within hours), while chloramination was slower (half-lives on the order of several days). MS ion scans revealed the formation of the four known BPA chlorinated by-products (BPA-Cl, BPA-2Cl, BPA-3Cl, BPA-4Cl) during the preliminary chlorination experiments. BADGE is unreactive with free chlorine and monochloramine.

A pseudo-first order kinetic model was developed to predict concentrations of BPA and BPF over time as a function of pH, temperature, and chlorine concentration. Based on experimental data and modeling efforts, the half-lives of BPA and BPF with 1 mg/L of free chlorine at pH 6 to 11 and temperatures of 10 and 25 °C are estimated to 3 to 35 min. The half-lives of BPA and BPF with a MCA concentration of 3.5 mg/L as Cl_2 at pH 7.6 to 9.1 and temperatures of 10 and 25 °C are estimated to be 1 to 10 days. The four known chlorinated BPA by-products were monitored during the experiments and were observed with both free chlorine and MCA. These half-lives are on timescales relevant to drinking water service lines, which often hold chlorinated water for extended periods of time.

6.3 Future Directions

Future research on this topic should include an investigation of additional linings and coatings materials. Investigation of additional epoxies (both BADGE- and BFDGE-based), other coating materials, and other lining materials would give a broader view of the potential for lining and coating technologies to leach organic chemicals into drinking water. Epoxy coatings and PET liners were the focus of this research because they are two of the most promising and commercially available technologies for use in small diameter drinking water service lines, but there are other organic lining and coating materials that could be used, including polyurethane, polyurea, polyethylene/epoxy, polyethylene, high-density polypropylene, and cross-linked polyethylene.

The fill-and-dump studies represented a worst-case scenario for leaching of organic constituents into drinking water exposed to linings and coatings because they involved a higher ratio of surface area to volume than other distribution system piping and because long holding times (stagnation periods) were used. Additional experiments should be done in which organic leachates are determined using shorter holding times and while water is actively flowing through the pipes, which would give a more accurate picture of the leachate concentrations to which consumers may be exposed over time. Another aspect that should be investigated is how the aging of linings or coatings affects the leaching of organic compounds.

Additional work should be done to elucidate structures of the unknown compounds (BADGE-H_2O-like and BPA-like compounds) observed during FD sampling. To determine if BADGE hydrolysis products are being detected as BPA-like compounds additional LC/MS precursor scans and Q1 scans should be done that include mass-to-charge values higher than

BPA. Standards of BADGE-H_2O and BADGE-$2H_2O$ should be analyzed with the LC/MS/MS bisphenol method. NMR data would also provide insight into the BPA-like compound structures, possibly confirming the proposed adducts or BADGE hydrolysis products. A larger volume (preparatory) column and fraction collection could help to obtain more concentrated samples of the BPA-like compounds. Determining the toxicity of the BPA-like compounds, with *e*strogenicity testing or computational methods *(*DEREK or TOPKAT) would help to identity if the health risks of these compounds are similar to that of BPA.

During the epoxy fill-and-dump experiments, a loss of chlorine was observed. The epoxy repeatedly exerted a significant and relatively rapid chorine demand. This interaction of free chlorine and epoxy has been observed in the literature but the exact mechanism of interaction is unknown (Chapter 2, Section 2.3.4.2). This interaction should be explored further to determine how long the chlorine demand lasts, if it is a reversible process, and if organic chloramines are being formed from the amines in the epoxy.

Some aspects of chlorinated by-product formation could be explored in more depth. The BPA and BPF half-lives with free chlorine are on timescales such that, if they were released in trace amounts from an epoxy coating, varying concentrations of their chlorinated by-products could form by the time the water reaches the faucet tap. Determining the toxicity (using estrogenicity tests or computational methods) of the chlorinated by-products, and monitoring for them at the tap downstream from existing applications of epoxy coatings, would be helpful in estimating human health risk. BADGE chlorination was not observed under drinking water conditions but there are reported BADGE chlorination by-products. Investigating

BADGE chlorination at high and low pH values would help in understanding conditions that facilitate chlorination.

Chlorination of BPA and BADGE with monochloramine should also be explored further. During the experiments examining BPA exposure to monochloramine, there was formation of BPA chlorinated by-products but the mass balance was not maintained. Additional investigations (MS Q1 scans) should be done to determine what else is being formed. In the study of BADGE exposure to monochloramine at pH 7, the BADGE hydrolysis by-products formed at rates different from those observed in the control solution (BADGE with no monochloramine). Mass spectrometry experiments (Q1 scans) with the solutions of BADGE by-products and MCA would aid in identifying structural changes influencing formation of the by-products. During the study of BADGE exposure to monochloramine at pH 9 there was an electrospray enhancement after two days of contact time. Exploring the electrospray enhancement in greater detail with MS Q1 scans could help to identify artifacts causing the enhancement.

Additional work should be done with the key chlorine by-products of bisphenol A and BADGE. Key by-products were monitored over the course of the experiments but long–term experiments, extending beyond decay of the key analytes, were not conducted. This type of investigation would help determine the longer term byproducts. MS Q1 scans should also be done with BPF and BFDGE to see if mono-, di- tri-, and tetra-chloro BPF and BFDGE-H_2O, BFDGE-$2H_2O$, BFDGE-H_2O-HCl, BFDGE-HCl, BFDGE-HCl are being formed.

Appendix: Supplemental Information and Standard Operating Procedures

A.1 Supplemental Information for Chapter 2: Organic Leachates from Drinking Water Service Line Liners and Coatings

A.1.1 Standard Operating Procedures for the Analysis of Bisphenols and Chlorinated Bisphenols by Liquid Chromatography Mass Spectrometry

Water Research Foundation Project 4351, Evaluation of Lead Service Line Lining and Coating Technologies, Version 1.1, February 28, 2013. Investigators (University of Kansas): Stephen J. Randtke, PI, Craig D. Adams, Co-PI, Edward F. (Ted) Peltier, Co-PI

A.1.1.1 Scope and Application

This SOP addresses the operating procedures for the analysis of drinking water by liquid chromatography with tandem mass spectrometry detection for bisphenol leachates from pipe linings and coatings.

Tables A.1.1.1 and A.1.1.2 list the main compounds to be analyzed but new analytes of interest may be added as the project progresses.

Table A.1.1.1 BP and Chlorinated BP Analyte List

Bisphenol A, (BPA)	**Suggested Internal Standard**
Bisphenol B, (BPB)	Bisphenol A-d16
Bisphenol D, (BPD)	
Bisphenol E, (BPE)	**Suggested Surrogate Internal Standard**
Bisphenol F, (BPF)	Bisphenol A-d8
Bisphenol S, (BPS)	
Tetrachloro bisphenol A, (BPA-4Cl)	

Table A.1.1.2 BP and Chlorinated BP Chemical Information

Abbreviation	Chemical Name	CAS Registry Number
BPA	4,4’-dihydroxydiphenyldimethylmethane	80-05-07
BPB	2,2-Bis(4-hydroxyphenyl)butane	77-40-7
BPD	4,4'-(1,3-Dimethylbutylidene)diphenol	6807-17-6
BPE	4,4'-Ethylidenebisphenol	2081-08-5
BPF	2,2'-methylenebis-phenol	620-92-8
BPS	Bis(4-hydroxyphenyl) sulfone	80-09-1
BPA-4Cl	2,2-Bis(3,5-dichloro-4-hydroxyphenyl)propane	79-95-8
BPA-D8	2,2-Bis(4-hydroxyphenyl-d4)propane	92739-58-7
BPA-D16	2,2-Bis(4-hydroxyphenyl)propane-d16	96210-87-6

A.1.1.2 Definitions

BP Bisphenol
IS Internal Standard
LC Liquid Chromatography
MCE Mixed cellulose ester
MDL Method Detection Limit
MRM Multiple Reaction Monitoring
MS Mass Spectrometry
Q1 Quadrupole 1 in the Mass Spectrometer
Q3 Quadrupole 3 in the Mass Spectrometer
R^2 Correlation coefficient
RR Relative Response
RT Retention Time
SIS Surrogate Internal Standard
SOP Standard Operating Procedure

A.1.1.3 Responsible Staff

Dr. Craig D. Adams, Co-PI
Dr. Stephen J Randtke, PI
Dr. Ray Carter, Research Associate
Dr. Karen Peltier, QA Project Manager
Ms. Rachael Lane, Graduate Research Assistant

A.1.1.4 Procedures

A.1.1.4.1 LC Preparation

The LC column is a Gemini-NX C18-with-TMS-endcapping column, 150 x 3.0 mm, 3-micron particle size (Phenomenex, Torrance, CA). Additional LC/MS instrument settings are listed in Table 3. Optima LC/MS grade water, free from BPs, was purchased from Fisher Scientific.

A.1.1.4.2 Sample Collection, Preservation, and Handling

Samples will be collected in glass bottles and clear glass 16 mL vials with PTFE lined caps. To reduce sorption of the analytes to the glass, each sample will be spiked with 10% methanol by volume (using Optima LC/MS grade methanol); a 16 mL sample has an addition of 1.6 mL methanol. Samples are run within 48 hours of arrival when possible, but if storage is required

the samples are stored in the dark at 5°C and analyzed as soon as possible. Record the time in days that the samples were stored.

A.1.1.4.3 Sample Specifications

To reduce sample contaminants, all samples are filtered with a Fisher MCE syringe filter. Prior to filtration, the SIS will be added such that percent recoveries can be calculated for the samples.

A.1.1.4.4 Analyte Identification

Analyte identification is confirmed though three parameters: Q1/Q3 ion pairs, ratio of the quantitation ion to the confirmation ion, and LC column retention time. These parameters are determined prior to samples analysis with analytical grade standards.

Table A.1.1.3 Recommended Instrument* Settings for BPs and Chlorinated BPs

Injection Volume	50 µL	
Mobile Phase A	LC/MS water	
Mobile Phase B	Methanol (Optima LC/MS grade)	
Gradient	1.0 min	65% B
	6.0 min	85% B
	12.0 min	85% B
	15.0 min	100% B
	17.0 min	100% B
	21.0 min	65% B
	26.0 min	65% B
	26.5 min	Stop
Integrated Valco Valve (Diverter)	0.1 min	To Waste
	3.0 min	To MS
	17.0 min	To Waste
MS Operating Mode	MRM	
Ionization Mode	Negative	
Nebulization Gas	Nitrogen	
MS Start Time	3.0 min	
MS End Time	12.0 min	
Collision cell exit potential (CXP), collision energy (CP), and the declustering potential (DP) values optimized for each analyte		

* API 4000Q Trap mass spectrometer (AB Sciex, Foster City, CA), equipped with a Shimadzu (Columbia, MD) Prominence HPLC, LC-20AB binary pump and SIL-20A autosampler

A.1.1.4.5 Instrument Calibration

For quantitation, the relationship between the instrument response and the bisphenol concentration should be linear. In addition to the initial calibration curves, the run method includes calibration checks and blanks to verify continued calibration.

A.1.1.4.5.1 Initial Calibration

Calibration standards are run at the start of a run method or every 24 hours. The initial calibration standards consists of the BP of interest, IS, and SIS. At least five calibration standards should be prepared with varying BP concentrations. The concentrations are chosen such that the sample BP concentration lies within the calibration curve. The lowest standard must be above two times the MDL (MDL calculated as outlined in *Standard Methods for the Examination of Water and Wastewater*), while the high concentration should be large enough to cover the desired BP range. Each concentration step should double from the prior concentration.

If the expected concentration in the sample is 20 µg/L, then the concentration of standards is: 5, 10, 20, 40, 80 µg/L. The lowest standard, 5 µg/L is greater than two times the MDL, the mid-range standard is the anticipated sample concentration, and the high standard is large enough to cover the desired range.

The SIS and IS are spiked into each of the calibration standards: SIS prior to filtration and IS after filtration (just prior to LC injection). The concentration of the IS and SIS must be the same in each calibration standard and sample. The IS and SIS concentration should be higher than that of the lowest calibration standard but not exceed that of the high calibration standard. In a run method with an expected BP sample concentration of 20 µg/L, the IS and SIS are spiked such that the concentration in every standard and sample is 20 µg/L.

A.1.1.4.5.2 Continuing Calibration

After every 10 samples a check standard is run. The check standard is the mid-range calibration standard. A blank is run before and after the standard to be sure carry over is not observed. Acceptance criterion is addressed in 4.5.4.3 (Continuing Calibration Checks).

A.1.1.4.5.3 Blanks

Blanks, consisting of BP-free LC/MS grade water, are run at the start and end of each run, before and after the check standard, and at least every 10 samples. Two blanks are placed at the start of a run method and the placing of blanks throughout the run method identifies carryover or contamination of the system. An example run order that includes initial calibration standards, check standards, blanks, and samples is shown in Table A.1.1.4. Each initial calibration standard should be run twice.

A.1.1.4.5.4 Matrix Spikes

Laboratory matrix spikes are used to establish if the sample matrix interferes with the method. A concentrated BP stock solution is spiked into a sample prior to syringe filtration. The final BP concentration in the spiked sample must not exceed the highest calibration standard. Each run method will have at least one matrix spike. For run methods with 40 or more samples the matrix spikes will be 5% of the total number of samples. For example a run method with 40 samples will have two matrix spikes; while a run method with 60 samples will have 3 matrix spikes.

A.1.1.4.5.5 Relative Response

The relative response (RR) is calculated for the analyte according to the following equation:

$$RR_a = A_a/A_{IS}$$

where: A_a = peak area of the analyte, A_{IS} = peak area of the internal standard

A.1.1.4.5.5.1 Calibration Curve from Relative Response

Calibration curves are constructed from the standards run at the start of each run method. The RR is calculated for the analyte and plotted as RR_a versus the known analyte concentration (C_a). From the best fit line, the correlation coefficient (R^2) must be ≥ 0.98 for a 5-point curve. If the criterion for the R^2 is not met, the calibration standards and all samples will be reanalyzed.

Table A.1.1.4 Example of Run Order with Samples having 20 µg/L Bisphenols

Sample Name	Description
Blank	LC/MS water
Blank1	LC/MS water
5 µg/L standard	Mix of BPs
5 µg/L standard	Mix of BPs
10 µg/L standard	Mix of BPs
10 µg/L standard	Mix of BPs
20 µg/L standard	Mix of BPs
20 µg/L standard	Mix of BPs
40 µg/L standard	Mix of BPs
40 µg/L standard	Mix of BPs
80 µg/L standard	Mix of BPs
80 µg/L standard	Mix of BPs
Blank2	LC/MS water
OP18-2012 06 28 Matrix Spike	Sample with BP addition
Blank3	LC/MS water
OP18-02-2012 06 28	Sample
OP18-03-2012 06 28	Sample
OP18-04-2012 06 28	Sample
OP18-04-2012 06 28DUP	Instrument duplicate
OP18-05-2012 06 28	Sample
OP18-06-2012 06 28	Sample
OP18-07-2012 06 28	Sample
OP18-08-2012 06 28	Sample
OP18-08-2012 06 28DUP	Instrument duplicate
Blank4	LC/MS water
20 µg/L standard	Check standard
Blank5	LC/MS water

Sample Labeling

Operators Initials Experiment Number-Sample Number-Date

OP18-01-2012 06 28

OP = Operators initials -01- = Sample Number

18 = Experiment Number 2012 06 28 = Date

A.1.1.4.5.5.2 Relative Response for Bisphenol Mixtures

When a sample or standard has multiple bisphenols, each peak will be integrated and the RR calculated for each analyte. The same criterion as described in 4.5.5.1 applies for each analyte.

A.1.1.4.5.5.3 Continuing Calibration Checks

The continuing calibration checks, run every 10 samples, are considered acceptable if they have less than 25% difference and the blanks run before and after the check standard show no carryover or contamination. The percent difference is calculated as follows:

$$\% \text{ difference} = (C_{aI} - C_a) / C_{aI} \times 100\%$$

where: C_{aI} = Analyte concentration from the initial calibration,

C_a = Analyte concentration from continuing calibration check

A.1.1.4.5.6 Sample Analysis Procedure

All samples are analyzed under the same LC/MS conditions as for the analytical standards. Sample concentrations must be within the range of the calibration standards used for the calibration curve.

A.1.1.4.5.6.1 Retention Time

The relative retention time of each analyte will be determined from the initial calibration standards on the day of analysis.

A.1.1.4.5.6.2 Minimum Peak Height

A signal-to-noise ratio of three is considered a relevant peak. A peak with a signal-to-noise ratio of three or less is considered noise.

A.1.1.5 Data Analysis

A.1.1.5.1 Data Recording

Appropriate method information and data will be recorded in a laboratory notebook. This notebook will be scanned, saved as a PDF document, and uploaded to the project file on the R drive. Everything analyzed on the LC/MS is logged in the LC/MS instrument notebook.

Data calculations and quantification and will be done with *Microsoft Excel*. The chromatograms and *Excel* files are backed up to the R drive and an external hard drive.

A.1.1.5.2 Sample Quantification

A.1.1.5.2.1 Quantification of Samples

The internal standard linear calibration curve is used to determine the concentrations of BPs in samples. The internal standard, BPA-D16, is added to the samples just prior to LC/MS injection (after any filtration).

A.1.1.5.2.2 Calibration Curve Construction

Using the parameters established in A.1.1.5.5, a calibration curve is constructed such that the y-axis is the relative response (A_A/A_{IS}) and the x-axis is the initial calibration standards concentration in µg/L,

where: A_A = peak area of the analyte in the initial calibration standard

A_{IS} = peak area of the IS in the initial calibration standard.

The equation of the line is calculated using a best fit line for at least 5 data points:

$$y = mx + b$$

where: m = slope and b = y-intercept

A.1.1.5.2.3 Concentration in sample

The relative response is calculated for each analyte in the sample. The concentration is calculated by substituting the relative response into the equation of the line and solving for concentration:

$$Concentration\ (\mu g/L) = [(A_{A\_sample}/A_{IS\_sample}) - b]/\ m$$

where: $A_{A\_samples}$ = peak area of the analyte in the samples

A_{IS_sample} = peak area of the IS in the initial calibration standard

A.1.1.5.2.4 Multicomponent Analysis

To quantitate multiple peaks: run analytical standards on LC/MS, use the Q1/Q3 ion pairs, ratio of the quantitation ion to confirmation ion, and retention time to confirm the specific analyte Calculate each analyte peaks as described in A.1.1.6.2.2.

A.1.1.5.3 Surrogate Internal Standard and Matrix Spike Recovery Calculations

A.1.1.5.3.1 Surrogate Recovery Calculations

Since the IS and SIS are spiked at the same concentration, the following equation is used to calculate the percent recovery of the surrogate from each sample:

$$\% \text{ Recovery} = [A_{SIS} / (\bar{x}RF_{SIS} \times A_{IS})] \times 100$$

where: A_{SIS} = peak area of the surrogate internal standard

A_{IS} = peak area of the internal standard

$\bar{x}RF_{SIS}$ = mean relative response factor of the surrogate internal standard

Variance of greater than 25% in SIS recovery between the standards and samples is considered significant, requiring that the problem be identified and corrected or the samples reanalyzed.

The relative response factor of the SIS is determined from the initial calibration standards:

$$RF_{SIS} = (A_{SIS} \times C_{IS}) / (C_{SIS} \times A_{IS})$$

where: A_{SIS} = peak area of the surrogate internal standard

A_{IS} = peak area of the internal standard

C_{SIS} = concentration of the surrogate internal standard in the initial calibration standard, in micrograms per liter

C_{IS} = concentration of the internal standard in the initial calibration standard, in micrograms per liter

After the RF_{SIS} is calculated for each initial calibration standard, the average is calculated as shown below:

$$\bar{x} = \frac{1}{n} \cdot \sum_{i=1}^{n} x_i$$

where: n = number of initial calibration standards

x_i = the RF_{SIS} value for each initial calibrations standards

This average $\bar{x}RF_{SIS}$ value is used in the % recovery equation.

A.1.1.5.3.2 Matrix Spike Recovery

The percent recovery of the matrix spike is calculated according to the following:

$$\% \text{ Matrix Recovery} = (C_{MS} - C_S) / C_{ADD}$$

where: C_{MS} = BP concentration in the spiked matrix sample

C_S = BP concentration in the original unspiked sample

C_{ADD} = the BP concentration that was spiked into the sample

If there is less than 75% recovery another quantitation method, such as standard additions, is required.

A.1.1.6 Quality Control

The specific quality control parameters are described in the following sections:

Instrument calibration standards & rejection parameters	Section A.1.1.4.5
Blanks	Section A.1.1.4.5.3
IS Spike and SIS Spike	Section A.1.1.4.2
Sample Peak Parameters	Section A.1.1.4.5.6
Data Recording	Section A.1.1.5.1
Surrogate and Matrix Spike Recovery	Section A.1.1.5.3

A.1.1.7 Safety

Standard laboratory safety practices will be followed including the use of protective clothing and eyeglasses and care when using flammable solvents.

A.1.1.8 Training

Prior to collecting any project-related data, each operator will be trained on the instrumentation and data entry, and will be required to demonstrate capability to obtain data of satisfactory quality.

A.1.1.9 References

APHA (American Public Health Association), AWWA (American Water Works Association), and WEF (Water Environment Federation), 2005. *Standard Methods for the Examination of Water and Wastewater, 21st ed.*, APHA, Washington, DC.

A.1.2 Analysis of bisphenol A diglycidyl ether (BADGE) by Liquid Chromatography Mass Spectrometry

Water Research Foundation Project 4351, Evaluation of Lead Service Line Lining and Coating Technologies, Version 1.0, September 2012. Investigators (University of Kansas): Stephen J. Randtke, PI, Craig D. Adams, Co-PI, Edward F. (Ted) Peltier, Co-PI

A.1.2.1 Scope and Application

This SOP addresses the operating procedures for the analysis of drinking water by liquid chromatography with tandem mass spectrometry detection of the bisphenol A diglycidyl ether leachate from pipe linings and coatings. Tables A.1.2.1 lists information about the analyte and suggested internal standard (SMXL-D4); other bisphenol diglycidyl ethers may be added as the project progresses.

Table A.1.2.1 Analyte and Suggested Internal Standard Information.

Name	Abbreviation	Chemical Name	CAS Number
bisphenol A diglycidyl ether	BADGE	2,2'-[(1-methylethylidene)bi(4,1-phenyleneoxymethylene)]bis-oxirane	1675-54-3
Sulfamethoxazole-D4	SMXL-D4	4-amino-N-(5-Methyl-3-isoxazolyl)(benzene-d4)sulfonamide	1020719-86-1

A.1.2.2 Definitions

IS Internal Standard
LC Liquid Chromatography
MDL Method Detection Limit
MRM Multiple Reaction Monitoring
MS Mass Spectrometry
Q1 Quadrupole 1 in the Mass Spectrometer
Q3 Quadrupole 3 in the Mass Spectrometer
R^2 Correlation coefficient
RR Relative Response
RT Retention Time
SOP Standard Operating Procedure

A.1.2.3 Responsible Staff

Dr. Craig D. Adams, Co-PI
Dr. Stephen J Randtke, PI
Dr. Ray Carter, Research Associate
Dr. Karen Peltier, QA Project Manager
Ms. Rachael Lane, Graduate Research Assistant

A.1.2.4 Procedures

A.1.2.4.1 LC Preparation

The LC column is a Gemini-NX C18-with-TMS-endcapping column, 150 x 3.0 mm, 3-micron particle size (Phenomenex, Torrance, CA). Additional LC/MS instrument settings are listed in Table A.1.1.2. LC/MS grade water and Optima LC/MS grade methanol, free from BADGE, was purchased from Fisher Scientific.

A.1.2.4.2 Sample Collection, Preservation, and Handling

Samples will be collected in glass bottles and clear glass 16 mL vials with PTFE lined caps. To reduce sorption of the analytes to the glass and hydrolysis, each sample will be spiked with 10% methanol (by volume); a 16 mL sample has an addition of 1.6 mL methanol. Samples are run within 48 hours of arrival when possible, but if storage is required the samples are stored in the dark at 5°C and analyzed as soon as possible. Record the time in days that the samples were stored.

A.1.2.4.3 Sample Specifications

An aliquot of sample will be taken, an appropriate amount of IS spiked, and the samples analyzed. Dilutions may be performed such that the samples concentration of BADGE does not exceed 400 µg/L.

A.1.2.4.4 Analyte Identification

Analyte identification is confirmed though three parameters: Q1/Q3 ion pairs, ratio of the quantitation ion to the confirmation ion, and LC column retention time. These parameters are determined, prior to sample analysis, with analytical grade standards.

A.1.2.4.5 Instrument Calibration

For quantitation, the relationship between the instrument response and BADGE concentration should be linear. In addition to the initial calibration curves, the run method includes calibration checks and blanks to verify continued calibration.

Table A.1.2.2 Recommended instrument settings for BADGE analysis.

Injection Volume	50 µL	
Mobile Phase A	LC/MS water with 25mM ammonium formate buffer at pH = 3.75	
Mobile Phase B	Methanol	
Gradient	0.5 min	30% B
	5.0 min	60% B
	10.0 min	84% B
	20.0 min	90% B
	25.0 min	100% B
	27.0 min	100% B
	32.0 min	60% B
	32.5 min	Stop
Integrated Valco Valve (Diverter)	0.1 min	To Waste
	1.0 min	To MS
	27.0 min	To Waste
MS Operating Mode	MRM	
Ionization Mode	Positive	
Nebulization Gas	Nitrogen	
MS Start Time	1.0 min	
MS End Time	27.0 min	
Collision cell exit potential (CXP), collision energy (CP), and the declustering potential (DP) values optimized for each analtye		
API 4000Q Trap mass spectrometer (AB Sciex, Foster City, CA), equipped with a Shimadzu (Columbia, MD) Prominence HPLC, LC-20AB binary pump, SIL-20A autosampler		

A.1.2.4.5.1 Initial Calibration

Calibration standards are run at the start of a run method or every 24 hours. The initial calibration standard consists of BADGE and the IS. At least five calibration standards should be prepared with varying BADGE concentrations. The concentrations are chosen such that the sample BADGE concentration lies within the calibration curve. The lowest standard must be above two times the MDL (MDL calculated as outlined in *Standard Methods for the Examination of Water and Wastewater*) and not lower that 25 µg/L. The LC/MS has a background BADGE peak and 25 µg/L is the concentration at which the signal to noise ratio is 2. The high concentration standard should be large enough to cover the desired BADGE range but not exceed 400 µg/L. Concentrations above 400 µg/L do not exhibit a linear response. Each concentration step should double from the prior concentration.

If the expected concentration in the sample is 100 µg/L, then the concentration of standards is: 25, 50, 100, 200, 400 µg/L. The lowest standard, 25 µg/L is greater than two times the MDL, the mid standard is the anticipated sample concentration, and the high standard is large enough to cover the desired range. A 0 µg/L BADGE sample will also be included that consists of LC/MS water with the internal standard.

The IS is spiked into each of the calibration standards just prior to LC injection. The concentration of the IS must be the same in each calibration standard and sample. The IS concentration should be higher than the lowest calibration standard and optimization indicates the SMXL-D4 concentration should be around 800 µg/L.

A.1.2.4.5.2 Continuing Calibration

After every 10 samples a check standard is run. The check standard is the mid-range calibration standard. A blank is run before and after the standard to be sure carry over is not observed. Acceptance criterion is addressed in 4.5.5.4 (Continuing Calibration Checks).

A.1.2.4.5.3 Blanks

Blanks, consisting of BADGE-free LC/MS grade water, are run at the start and end of each run, after each standard, before and after the check standard, and after every sample. The increased frequency of blanks allow for the background BADGE peak to be monitored. Two

blanks are placed at the start of a run method and the placing of blanks throughout the run method identifies carryover or contamination of the system. An example of a run order is shown in Table A.1.2.3.

A.1.2.4.5.4 Matrix Spikes

Laboratory matrix spikes are used to establish if the sample matrix interferes with the method. A concentrated BADGE stock solution is spiked into a sample prior to LC injection. The final BADGE concentration in the spiked sample must not exceed the highest calibration standard. Each run method will have at least one matrix spike. For run methods with 40 or more samples the matrix spikes will be 5% of the total number of samples. For example a run method with 40 samples will have two matrix spikes; while a run method with 60 samples will have 3 matrix spikes. An example run order that includes initial calibration standards, check standards, blanks, matrix spikes, and samples is shown in Table A.1.2.3. Each initial calibration standard should be run twice.

A.1.2.4.5.5 Relative Response

The stability the BADGE background level will determine how the relative response is calculated. If the level is relatively stable, the data will be background corrected.

A.1.2.4.5.5.1 Relative Response with Background Correction

The average peak area of all the blanks will be calculated along with the standard deviation calculated (equations shown below).

$$\bar{x} = \frac{1}{n} \cdot \sum_{i=1}^{n} x_i$$

where: $\bar{x}$ = mean (average) BADGE peak area of the blanks

n = number of blanks

x_i = BADGE peak areas of each blank

$$s = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \overline{x})^2}$$

where: s = standard deviation of the blanks

$\bar{x}$ = mean (average) of the blanks

N = number of blanks

x_i = BADGE peak areas of each blank

From the two values, a percent relative standard deviation is calculated:

%RSD = (s/ $\bar{x}$)*100%

If the %RSD is less than 10%, the data is background corrected

The relative response (RR) for the background corrected data is calculated according to the following equation:

$$RR_{BADGE} = (A_{BADGE} - \bar{x}\ )/A_{IS}$$

where: $\bar{x}$ *= mean (average) BADGE peak area of the blanks*

A_{BADGE} = peak area of the BADGE

A_{IS} = peak area of the internal standard

A.1.2.4.5.5.2 Relative Response without Background Correction

If the calculated %RSD of the blanks is greater than 10%, the data will not be background corrected and the RR is calculated as follows:

$$RR_{BADGE} = (A_{BADGE})/A_{IS}$$

where: A_{IS} = peak area of the internal standard

A_{BADGE} = peak area of the BADGE

A.1.2.4.5.5.3 Calibration Curve from Relative Response

Calibration curves are constructed from the standards run at the start of each run method. The RR is calculated for the analyte and plotted as RR_a versus the known analyte concentration (C_a). From the best fit line, the correlation coefficient (R^2) must be ≥ 0.98 for a 5-point curve. If the criterion for the R^2 is not met, the calibration standards and all samples will be reanalyzed.

Table A.1.2.3 Example of run order with samples having 100 µg/L BADGE.

Sample Name	Description
Blank1	LC/MS water
Blank2	LC/MS water
0 µg/L standard	LC/MS water with IS
0 µg/L standard	LC/MS water with IS
Blank3	LC/MS water
25 µg/L standard	BADGE
25 µg/L standard	BADGE
Blank4	LC/MS water
50 µg/L standard	BADGE
50 µg/L standard	BADGE
Blank5	LC/MS water
100 µg/L standard	BADGE
100 µg/L standard	BADGE
Blank6	LC/MS water
200 µg/L standard	BADGE
200 µg/L standard	BADGE
Blank7	LC/MS water
400 µg/L standard	BADGE
400 µg/L standard	BADGE
Blank8	LC/MS water
OP18-2012 06 28 Matrix Spike	Sample with BADGE addition
Blank9	LC/MS water
OP18-02-2012 06 28	Sample
OP18-03-2012 06 28	Sample
Blank10	LC/MS water
OP18-04-2012 06 28	Sample
OP18-04-2012 06 28DUP	Instrument duplicate
Blank11	LC/MS water
OP18-05-2012 06 28	Sample
OP18-06-2012 06 28	Sample
Blank12	LC/MS water
OP18-07-2012 06 28	Sample
OP18-08-2012 06 28	Sample
OP18-08-2012 06 28DUP	Instrument duplicate
Blank13	LC/MS water
100 µg/L standard	BADGE
Blank14	LC/MS water

Sample Labeling

Operators Initials Experiment Number-Sample Number-Date

OP18-01-2012 06 28

OP = Operators initials -01- = Sample Number

18 = Experiment Number 2012 06 28 = Date

A.1.2.4.5.5.4 Continuing Calibration Checks

The continuing calibration checks, run every 10 samples, are considered acceptable if they have less than 25% difference and the blanks run before and after the check standard show no carryover or contamination. The percent difference is calculated as follows:

$$\% \text{ difference} = (C_{aI} - C_a) / C_{aI} \times 100\%$$

where: C_{aI} = Analyte concentration from the initial calibration

C_a = Analyte concentration from continuing calibration check

A.1.2.4.5.6 Sample Analysis Procedure

All samples are analyzed under the same LC/MS conditions as for the analytical standards. Sample concentrations must be within the range of the calibration standards used for the calibration curve.

A.1.2.4.5.6.1 Retention Time

The relative retention time of each analyte will be determined from the initial calibration standards on the day of analysis.

A.1.2.4.5.6.2 Minimum Peak Height

A signal-to-noise ratio of two is considered a relevant peak. A peak with a signal-to-noise ratio of two or less is considered noise.

A.1.2.5 Data Analysis

A.1.2.5.1 Data Recording

Appropriate method information and data will be recorded in a laboratory notebook. This notebook will be scanned, saved as a PDF document, and uploaded to the project file on the R drive (School of Engineering hard drive for research projects). Everything analyzed on the LC/MS is logged in the LC/MS instrument notebook. Data calculations and quantification and will be done with *Microsoft Excel*. The chromatograms and *Excel* files are backed up to the R drive and an external hard drive.

A.1.2.5.2 Sample Quantification

The internal standard linear calibration curve is used to determine the concentrations of BADGE in samples. The internal standard, SMXL-D4, is added to the samples just prior to LC/MS injection.

A.1.2.5.2.1 Calibration Curve Construction

Using the parameters established in A.1.2.4.5, a calibration curve is constructed such that the y-axis is the relative response, A_A/A_{IS} or $(A_{BADGE} - \bar{x})/A_{IS}$, and the x-axis is the initial calibration standards concentration in µg/L. The equation of the line is calculated using a best fit line for at least 5 data points:

$$y = mx + b$$

where: m = slope and b = y-intercept

A.1.2.5.2.2 Concentration in sample

The relative response is calculated for each analyte in the sample. If the standards are background corrected, than the samples must also be background corrected. The concentration is calculated by substituting the relative response into the equation of the line and solving for concentration:

Background Correction

$$Concentration\ (\mu g/L) = [(A_{A\_sample} - \bar{x})//A_{IS\_sample}) - b]/\ m$$

where: A_{A_sample} = BADGE peak area in the sample

A_{IS_sample} = peak area of the IS in the sample

No Background Correction

$$Concentration\ (\mu g/L) = [(A_{A\_sample}/A_{IS\_sample}) - b]/\ m$$

where: $A_{A\_samples}$ = peak area of the analyte in the samples

A_{IS_sample} = peak area of the IS in the sample

A.1.2.5.3 Matrix Spike Recovery Calculations

The percent recovery of the matrix spike is calculated according to the following:

$$\% \text{ Matrix Recovery} = (C_{MS} \times C_S) / C_{ADD}$$

where: C_{MS} = BADGE concentration in the spiked matrix sample

C_S = BADGE concentration in the sample

C_{ADD} = the BADGE concentration that was spiked into the sample

If there is less than 75% recovery another quantitation method, such as standard additions, is required.

A.1.2.6 Quality Control

The specific quality control parameters are described in the following sections:

Instrument calibration standards & rejection parameters	Section A.1.2.4.5.1 to A.1.2.4.5.4
Blanks	Section A.1.2.4.5.3
IS Spike	Section A.1.2.4.5.1
Sample Peak Parameters	Section A.1.2.4.5.6
Background Correction	Section A.1.2.4.5.5
Data Recording	Section A.1.2.5.1
Matrix Spike Recovery	Section A.1.2.5.3

A.1.2.7 Safety

Standard laboratory safety practices will be followed including the use of protective clothing and eyeglasses and care when using flammable solvents.

A.1.2.8 Training

Prior to collecting any project-related data, each operator will be trained on the instrumentation and data entry, and will be required to demonstrate capability to obtain data of satisfactory quality.

A.1.2.9 References

APHA (American Public Health Association), AWWA (American Water Works Association), and WEF (Water Environment Federation), 2005. *Standard Methods for the Examination of Water and Wastewater, 21st ed.*, APHA, Washington, DC.

A.1.3 Analysis of Phthalic Acids by Liquid Chromatography Mass Spectrometry

Water Research Foundation Project 4351, Evaluation of Lead Service Line Lining and Coating Technologies, Version 1.0, May 2013. Investigators (University of Kansas): Stephen J. Randtke, PI, Craig D. Adams, Co-PI, Edward F. (Ted) Peltier, Co-PI

A.1.3.1 Scope and Application

This SOP addresses the operating procedures for the analysis of drinking water by liquid chromatography with tandem mass spectrometry detection for phthalic acid leachates from PET (polyethylene terephthalate) linings and coatings. Tables A.1.3.1 and Table A.1.3.2 list the main compounds to be analyzed.

Table A.1.3.1 Phthalic Acids Analyte List

Phthalic Acid, (PA)	**Suggested Internal Standard**
Isophthalic Acid, (IPA)	Phthalic Acid-D4 (PA-D4)
Terephthalic Acid, (TPA)	

Table A.1.3.2 Phthalic Acid Chemical Information

Abbreviation	Chemical Name	CAS Registry Number
PA	Benzene-1,2-dicarboxylic acid	88-99-3
IPA	Benzene-1,3-dicarboxylic acid	212-91-5
TPA	Benzene-1,4-dicarboxylic acid	100-21-0
PA-D4	Benzene-1,2-dicarboxylic acid-phenyl-d4	87976-26-9

A.1.3.2 Definitions

IS Internal Standard
LC Liquid Chromatography
MCE Mixed cellulose ester
MDL Method Detection Limit
MRM Multiple Reaction Monitoring
MS Mass Spectrometry
PA Phthalic Acids
Q1 Quadrupole 1 in the Mass Spectrometer
Q3 Quadrupole 3 in the Mass Spectrometer
R^2 Correlation coefficient
RR Relative Response
RT Retention Time
SIS Surrogate Internal Standard
SOP Standard Operating Procedure

A.1.3.3 Responsible Staff

Dr. Craig D. Adams, Co-PI
Dr. Stephen J Randtke, PI
Dr. Ray Carter, Research Associate
Dr. Karen Peltier, QA Project Manager
Ms. Rachael Lane, Graduate Research Assistant

A.1.3.4 Procedures

A.1.3.4.1 LC Preparation

The LC column is a Gemini-NX C18-with-TMS-endcapping column, 150 x 3.0 mm, 3-micron particle size (Phenomenex, Torrance, CA). Additional LC/MS instrument settings are listed in Table 3. Optima LC/MS grade water, free from PA, was purchased from Fisher Scientific.

A.1.3.4.2 Sample Collection, Preservation, and Handling

Samples will be collected in glass bottles and amber glass 40 mL vials with PTFE lined caps. To reduce sorption of the analytes to the glass, each sample will be spiked with 10% acetonitrile by volume (using Optima HPLC grade acetonitrile); a 16 mL sample has an addition of 1.6 mL methanol. Samples are run within 48 hours of arrival when possible, but if storage is required the samples are stored in the dark at 5°C and analyzed as soon as possible. Record the time in days that the samples were stored.

Care must be taken during sample preparation and handling to reduce environmental phthalate contamination. All glassware should be rinsed with acetonitrile and plastics should be avoided.

A.1.3.4.3 Analyte Identification

Analyte identification is confirmed though two parameters: Q1/Q3 ion pairs and LC column retention time. Since the analytes are isomers the retention time must be verified an analytical grade standard of each phthalic acid.

Table A.1.3.3 Recommended Instrument* Settings for Phthalic Acids

Injection Volume	25 µL	
Mobile Phase A	LC/MS water (with 0.1% formic acid)	
Mobile Phase B	Acetonitrile	
Flow Rate	0.4 mL/min	
Gradient	1.0 min	15% B
	2.0 min	15% B
	9.8 min	36% B
	20.0 min	49% B
	22.0 min	100% B
	24.0 min	100% B
	29.0 min	15% B
	29.5 min	Stop
Integrated Valco Valve (Diverter)	0.1 min	To Waste
	5.0 min	To MS
	22.0 min	To Waste
MS Operating Mode	MRM	
Ionization Mode	Negative	
Nebulization Gas	Nitrogen	
Entrance Potential	-10.0	
Curtain Gas	20.0	
MS Start Time	3.0 min	
MS End Time	12.0 min	
MS Mass/Charge Values for MRM		
Q1→Q3 Mass PA Quantitation Ion	165.000 → 120.908	
Q1→Q3 Mass PA Confirmation Ion	165.000 → 77.108	
Q1→Q3 Mass PA-D4 Quantitation Ion	169.160 → 81.100	
Q1→Q3 Mass PA-D4 Confirmation Ion	169.160 → 124.894	
Collision cell exit potential (CXP), collision energy (CP), and the declustering potential (DP) values optimized for each analyte		

* API 4000Q Trap mass spectrometer (AB Sciex, Foster City, CA), equipped with a Shimadzu (Columbia, MD) Prominence HPLC, LC-20AB binary pump and SIL-20A autosampler

A.1.3.4.4 Instrument Calibration

For quantitation, the relationship between the instrument response and the phthalic acid concentration should be linear. In addition to the initial calibration curves, the run method includes calibration checks and blanks to verify continued calibration.

A.1.3.4.4.1 Initial Calibration

Calibration standards are run at the start of a run method or every 24 hours. The initial calibration standards consists of the PA of interest, IS, and SIS. At least five calibration standards should be prepared with varying PA concentrations. The concentrations are chosen such that the sample PA concentration lies within the calibration curve. The lowest standard must be above two times the MDL (MDL calculated as outlined in *Standard Methods for the Examination of Water and Wastewater*), while the high concentration should be large enough to cover the desired PA range. Each concentration step should double from the prior concentration.

If the expected concentration in the sample is 20 µg/L, then the concentration of standards is: 5, 10, 20, 40, 80 µg/L. The lowest standard, 5 µg/L is greater than two times the MDL, the mid-range standard is the anticipated sample concentration, and the high standard is large enough to cover the desired range.

The IS is spiked into each of the calibration standards just prior to LC injection and the concentration of the IS must be the same in each calibration standard and sample. The IS concentration should be higher than that of the lowest calibration standard but not exceed that of the high calibration standard.

A.1.3.4.4.2 Continuing Calibration

After every 10 samples a check standard is run. The check standard is the mid-range calibration standard. A blank is run before and after the standard to be sure carry over is not observed. Acceptance criterion is addressed in section A.1.3.4.4.5.3 (Continuing Calibration Checks).

A.1.3.4.4.3 Blanks

Blanks, consisting of PA-free LC/MS grade water, are run at the start and end of each run, before and after the check standard, and at least every 10 samples. Two blanks are placed at the start of a run method and the placing of blanks throughout the run method identifies carryover or contamination of the system. An example run order that includes initial calibration standards, check standards, blanks, and samples is shown in Table A.1.3.4. Each initial calibration standard should be run twice. An example of a run order is shown in Table A.1.3.4.

A.1.3.4.4.4 Matrix Spikes

Laboratory matrix spikes are used to establish if the sample matrix interferes with the method. A concentrated PA stock solution is spiked into a sample prior injection. The final PA concentration in the spiked sample must not exceed the highest calibration standard. Each run method will have at least one matrix spike. For run methods with 40 or more samples the matrix spikes will be 5% of the total number of samples. For example a run method with 40 samples will have two matrix spikes, while a run method with 60 samples will have 3 matrix spikes.

A.1.3.4.4.5 Relative Response

The relative response (RR) is calculated for the analyte according to the following equation:

$$RR_a = A_a/A_{IS}$$

where: A_a = peak area of the analyte

A_{IS} = peak area of the internal standard

A.1.3.4.4.5.1 Calibration Curve from Relative Response

Calibration curves are constructed from the standards run at the start of each run method. The RR is calculated for the analyte and plotted as RR_a versus the known analyte concentration (C_a). From the best fit line, the correlation coefficient (R^2) must be ≥ 0.98 for a 5-point curve. If the criterion for the R^2 is not met, the calibration standards and all samples will be reanalyzed.

Table A.1.3.4 Example of run order with samples having 20 µg/L phthalic acid

Sample Name	**Description**
Blank	LC/MS water
Blank1	LC/MS water
0 µg/L standard	control
0 µg/L standard	control
5 µg/L standard	Mix of PAs
5 µg/L standard	Mix of PAs
10 µg/L standard	Mix of PAs
10 µg/L standard	Mix of PAs
20 µg/L standard	Mix of PAs
20 µg/L standard	Mix of PAs
40 µg/L standard	Mix of PAs
40 µg/L standard	Mix of PAs
80 µg/L standard	Mix of PAs
80 µg/L standard	Mix of PAs
Blank2	LC/MS water
OP18-2012 06 28 Matrix Spike	Sample with PA addition
Blank3	LC/MS water
OP18-02-2012 06 28	Sample
OP18-03-2012 06 28	Sample
OP18-04-2012 06 28	Sample
OP18-04-2012 06 28DUP	Instrument duplicate
OP18-05-2012 06 28	Sample
OP18-06-2012 06 28	Sample
OP18-07-2012 06 28	Sample
OP18-08-2012 06 28	Sample
OP18-08-2012 06 28DUP	Instrument duplicate
Blank4	LC/MS water
20 µg/L standard	Check standard
20 µg/L PA	Retention Time Determination
20 µg/L IPA	Retention Time Determination
20 µg/L TPA	Retention Time Determination
Blank5	LC/MS water

Sample Labeling

Operators Initials Experiment Number-Sample Number-Date

OP18-01-2012 06 28

OP = Operators initials -01- = Sample Number

18 = Experiment Number 2012 06 28 = Date

A.1.3.4.4.5.2 Relative Response for Phthalic Acid Mixtures

When a sample or standard has multiple phthalic acids, each peak will be integrated and the RR calculated for each analyte. The same criterion as described in section A.1.3.4.4.5.1 applies for each analyte.

A.1.3.4.4.5.3 Continuing Calibration Checks

The continuing calibration checks, run every 10 samples, are considered acceptable if they have less than 25% difference and the blanks run before and after the check standard show no carryover or contamination. The percent difference is calculated as follows:

$$\% \text{ difference} = (C_{aI} - C_a) / C_{aI} \times 100\%$$

where: C_{aI} = Analyte concentration from the initial calibration

C_a = Analyte concentration from continuing calibration

A.1.3.4.4.6 Sample Analysis Procedure

All samples are analyzed under the same LC/MS conditions as for the analytical standards. Sample concentrations must be within the range of the calibration standards used for the calibration curve.

A.1.3.4.4.6.1 Retention Time

The relative retention time of each analyte will be determined from the initial calibration standards on the day of analysis.

A.1.3.4.4.6.2 Minimum Peak Height

A signal-to-noise ratio of three is considered a relevant peak. A peak with a signal-to-noise ratio of three or less is considered noise.

A.1.3.5 Data Analysis

Appropriate method information and data will be recorded in a laboratory notebook. This notebook will be scanned, saved as a PDF document, and uploaded to the project file on the R drive. Everything analyzed on the LC/MS is logged in the LC/MS instrument notebook. Data calculations and quantification and will be done with *Microsoft Excel*. The chromatograms and *Excel* files are backed up to the R drive and an external hard drive.

A.1.3.5.1 Sample Quantification

The internal standard linear calibration curve is used to determine the concentrations of PAs in samples. The internal standard, PA-D4, is added to the samples just prior to LC/MS injection. The quantification of the samples will be done with a linear calibration curve.

A.1.3.5.1.1 Calibration Curve Construction

Using the parameters established in section A.1.3.4.4, a calibration curve is constructed such that the y-axis is the relative response (A_A/A_{IS}) and the x-axis is the initial calibration standards concentration in µg/L.

$$\text{relative response} = (A_A/A_{IS})$$

where: A_A = peak area of the analyte in the initial calibration standard

A_{IS} = peak area of the IS in the initial calibration standard

The equation of the line is calculated using a best fit line for at least 5 data points:

$$y = mx + b$$

where: m = slope and b = y-intercept

A.1.3.5.1.2 Concentration in sample

The relative response is calculated for each analyte in the sample. The concentration is calculated by substituting the relative response into the equation of the line and solving for concentration:

$$\text{Concentration } (\mu g/L) = [(A_{A\_sample}/A_{IS\_sample}) - b]/\, m$$

where: $A_{A\_samples}$ = peak area of the analyte in the samples

A_{IS_sample} = peak area of the IS in the initial calibration standard

A.1.3.5.3.3 Multicomponent Analysis

The process described in section A.1.3.5.1 for a single peak can be applied to a chromatogram with multiple peaks. To quantitate multiple peaks: run analytical standards on LC/MS, use the Q1/Q3 ion pairs and retention time to confirm the specific analyte, calculate each analyte peaks as described in section A.1.3.5.1.

A.1.3.5.2 Matrix Spike Recovery Calculations

The percent recovery of the matrix spike is calculated according to the following:

$$\% \text{ Matrix Recovery} = (C_{MS} - C_S) / C_{ADD}$$

where: C_{MS} = PA concentration in the spiked matrix sample

C_S = PA concentration in the original unspiked sample

C_{ADD} = the PA concentration that was spiked into the sample

If there is less than 75% recovery another quantitation method, such as standard addition, is required.

A.1.3.6 Quality Control

The specific quality control parameters are described in the following sections:

Instrument calibration standards & rejection parameter	Section A.1.3.4.4 to A.1.3.4.4.4
Blanks	Section A.1.3.4.4.3
IS Spike	Section A.1.3.4.4
Sample Peak Parameters	Section A.1.3.4.4.6
Data Recording	Section A.1.3.4.1
Matrix Spike Recovery	Section A.1.3.4.2

A.1.3.7 Safety

Standard laboratory safety practices will be followed including the use of protective clothing and eyeglasses and care when using flammable solvents.

A.1.3.8 Training

Prior to collecting any project-related data, each operator will be trained on the instrumentation and data entry, and will be required to demonstrate capability to obtain data of satisfactory quality.

A.1.3.9 References

APHA (American Public Health Association), AWWA (American Water Works Association), and WEF (Water Environment Federation), 2005. *Standard Methods for the Examination of Water and Wastewater, 21st ed.*, APHA, Washington, DC

A.1.4 Signal-to-Noise Determination for LC/MS/MS and GC/MS Analysis

The Signal-to-Noise Ratio (S/N) is a way to distinguish the analyte signal from background noise. Analytically the goal is to reduce background noise as much as possible but it cannot be completely eliminated. The general recommendation is that a S/N above 2 or 3 is considered significant, while a value below that is regarded as noise.[1]

A.1.4.1 Calculation of the Signal-to-Noise (S/N)

Some software packages will calculate the S/N for peaks and can be used in place of the method described below. If software calculation is not available a method for determine of the S/N is described below.

For the calculation, run a blank sample (matrix solution used for the standards but with no analytes spiked into it) and a standard or sample. Noise is defined as the baseline max to min peak height near the elution time of the analyte. The analyte peak is then defined as the height from the mean noise level to top of peak. The S/N calculated according to the following equation:

$$\frac{S}{N} = \frac{\left(H_{analyte} - H_{NoiseMean}\right)}{H_{NoiseMax}}$$

where: $H_{analyte}$ = peak height of the analyte in the standard (or sample), $H_{NoiseMax}$ = The maximum peak height in the control right around the elution time of the analyte, $H_{NoiseMean}$ = The average peak height of the noise in the control right around the elution time of the analyte

In the following data provided as an example, the peak starting at 6.9394 to 7.4227 min is considered a relevant analyte (BPA) signal and all other values in the BPA standard are considered noise.

A.1.4.2 Reference

1. Skoog, D. A.; Holler, F. J.; Crouch, S. R., Chapter 5 Signals and Noise. In *Principles of Instrumental Analysis*, 6th ed.; Thomson Brooks/Cole: Belmont, CA, 2007; pp 110-130.

Table A.1.4.1 Blank and sample data for the determination of S/N values.

LC/MS/MS Chromatogram Data for Blank				LC/MS/MS Chromatogram Data for Bisphenol A Standard					
Time	Intensity	Time	Intensity	Time	Intensity	S/N	Time	Intensity	S/N
6.5192	20	7.2756	30	6.5192	130	1.4	7.2756	1550	22
6.5402	20	7.2966	20	6.5402	100	1.0	7.2966	880	12
6.5612	0	7.3176	60	6.5612	140	1.6	7.3176	500	6.7
6.5822	10	7.3386	50	6.5822	130	1.4	7.3386	560	7.6
6.6032	30	7.3596	10	6.6032	140	1.6	7.3596	490	6.6
6.6242	50	7.3806	0	6.6242	100	1.0	7.3806	350	4.6
6.6452	40	7.4016	40	6.6452	80	0.7	7.4016	320	4.1
6.6662	50	7.4227	20	6.6662	140	1.6	7.4227	290	3.7
6.6872	20	7.4437	30	6.6872	70	0.6	7.4437	150	1.7
6.7083	20	7.4647	0	6.7083	120	1.3	7.4647	140	1.6
6.7293	10	7.4857	40	6.7293	120	1.3	7.4857	240	3.0
6.7503	0	7.5067	10	6.7503	80	0.7	7.5067	190	2.3
6.7713	20	7.5277	70	6.7713	70	0.6	7.5277	220	2.7
6.7923	30	7.5487	10	6.7923	110	1.1	7.5487	100	1.0
6.8133	30	7.5697	40	6.8133	30	0.0	7.5697	110	1.1
6.8343	60	7.5907	50	6.8343	130	1.4	7.5907	170	2.0
6.8553	40	7.6117	30	6.8553	90	0.9	7.6117	130	1.4
6.8764	20	7.6328	0	6.8764	80	0.7	7.6328	120	1.3
6.8974	30	7.6538	20	6.8974	80	0.7	7.6538	120	1.3
6.9184	60	7.6748	0	6.9184	210	2.6	7.6748	130	1.4
6.9394	20	7.6958	0	6.9394	930	13	7.6958	50	0.3
6.9604	40	7.7168	0	6.9604	2370	33	7.7168	160	1.9
6.9814	60	7.7378	40	6.9814	5280	75	7.7378	100	1.0
7.0024	20	7.7588	30	7.0024	9380	134	7.7588	90	0.9
7.0234	30	7.7798	10	7.0234	14110	201	7.7798	100	1.0
7.0445	30	7.8008	20	7.0445	17090	244	7.8008	70	0.6
7.0655	40	7.8219	30	7.0655	19320	276	7.8219	160	1.9
7.0865	60	7.8429	20	7.0865	20460	292	7.8429	110	1.1
7.1075	70	7.8639	20	7.1075	21540	307	7.8639	130	1.4
7.1285	40	7.8849	70	7.1285	19830	283	7.8849	120	1.3
7.1495	70	7.9059	30	7.1495	17550	250	7.9059	170	2.0
7.1705	30	7.9269	20	7.1705	12430	177	7.9269	110	1.1
7.1915	30	7.9479	10	7.1915	8560	122	7.9479	100	1.0
7.2125	50	7.969	10	7.2125	5620	80	7.969	100	1.0
7.2336	0	7.99	30	7.2336	3580	51	7.99	80	0.7
7.2546	50	8.011	10	7.2546	2200	31	8.011	90	0.9
Median ($H_{NoiseMean}$): 30 **Max ($H_{NoiseMax}$): 70**				$\frac{S}{N} = \frac{(H_{analyte} - H_{NoiseMean})}{H_{NoiseMax}} = \frac{(130 - 30)}{70} = 1.4$					

A.1.5 Analysis of Phthalates Esters by Gas Chromatography Mass Spectrometry

Water Research Foundation Project 4351, Evaluation of Lead Service Line Lining and Coating Technologies, Version 1.0, May 2013. Investigators (University of Kansas): Stephen J. Randtke, PI, Craig D. Adams, Co-PI, Edward F. (Ted) Peltier, Co-PI

A.1.5.1 Scope and Application

This SOP addresses the operating procedures for the drinking water analysis by gas chromatography with mass spectrometry detection of phthalate esters leached from pipe coatings. Tables A.1.5.1 and A.1.5.2 list the compounds to be analyzed but new analytes of interest may be added as the project progresses.

A.1.5.2 Definitions

IS	Internal Standard
SIS	Surrogate Internal Standard
GC	Gas Chromatography
MDL	Method Detection Limit
MS	Mass Spectrometry
R^2	Correlation coefficient
RR	Relative Response
RT	Retention Time
SOP	Standard Operating Procedure
S/N	Signal-to-Noise value

A.1.5.3 Responsible Staff

Dr. Craig D. Adams, Co-PI
Dr. Stephen J Randtke, PI
Dr. Ray Carter, Research Associate
Dr. Karen Peltier, QA Project Manager
Ms. Rachael Lane, Graduate Research Assistant

Table A.1.5.1 Phthalate esters of interest and suggested internal and surrogate standards.

Butyl benzyl phthalate, (BBP) Bis(2-ethylhexyl) adipate, (DEHA) Di ethyl hexyl phthalate, (DEHP) Diethyl phthalate, (DEP) Diethyl terephthalate, (DETP) Dimethyl isophthalate, (DMIP) Dimethyl phthalate, (DMP) Dimethyl terephthalate, (DMTP) Di-n-butyl phthalate, (DNBP) Di-n-octyl phthalate, (DNOP)	**Suggested Internal Standard** phenanthrene-D10 (PANE-D10) **Suggested Surrogate Internal Standard** dihexyl phthalate-D6 (DNHP-d6)

Table A.1.5.2 Chemical information for phthalate esters.

Abbreviation	Chemical Name	CAS Registry Number
BBP	1,2-benzenedicarboxylic acid, butyl phenylmethyl ester	85-68-7
DEHA	bis(2-ethylhexyl)hexanedioate	103-23-1
DEHP	1,2-benzenedicarboxylic acid, bis(2-ethylhexyl) ester	117-81-7
DEP	1,2-benzenedicarboxylic acid diethyl ester	84-66-2
DETP	1,4-benzenedicarboxylic acid, diethyl ester	636-09-9
DMIP	1,3-benzenedicarboxylicacid,dimethylester	1459-93-4
DMP	1,2-benzendicarboxylicacid,dimethylester	131-11-3
DMTP	1,4-benzenedicarboxylicacid,dimethylester	120-61-6
DNBP	benzene-1,2-dicarboxylicaciddibutylester	84-74-2
DNOP	1,2-benzenedicarbonic acid, dioctyl ester	117-84-0
PANE-D10	decadeutero- (o-diphenylenethylene)	1517-22-2
DNHP-D6	(phthalic acid di-n-hexyl ester)-3,4,5,6-d4	1015854-55-3

A.1.5.4 Procedures

A.1.5.4.1 GC Preparation

The GC column is a Varian FactorFour Capillary Column VF-5MS 30 m x 0.32 mm (i.d.) composed of a highly inert, 5% phenylmethylpolysiloxane phase with 0.5 µm film thickness. The septum of the GC injector is changed after approximately 100 injections. Additional GC/MS instrument settings are listed in Table A.1.5.3. HPLC grade hexanes and chloroform will be used as the solvents.

Table A.1.5.3 Recommended GC/MS instument settings for analysis of phthalate esters.

Column	Varian FactorFour Capillary Column VF-5MS 30m × 0.32mm × 0.5µm
Injection	1.0µL splitless
Injection Temperature	270°C isothermal
Carrier Gas	helium
Flow Rate	1.0mL/min constant flow
Transfer Line Temperature	270°C isothermal
Oven Temperature	120°C (hold for 0 minute) Ramp at 20°C/min to 200°C Ramp at 30°C/min to 220°C Ramp at 10°C/min to 250°C 250°C (hold for 6 minutes) Ramp at 10°C/min to 300°C 300°C (hold for 4 minutes)
Solvent Delay	4.5 min
Solvent	Hexanes/Chloroform (50/50 by volume)
MS Ions Monitored	4.5 – 7.7 min 163.1 & 194.1 amu 7.7 – 10.0 min 149.1 & 177.1 amu 10.0 – 12.6 min 160.0 & 188.2 amu 12.6 - 18.0 min 149.1 & 223.1 amu 18.0 – 20.6 min 153.1 & 255.1 amu 20.6 – 21.0 min 149.1 & 206.1 amu 21.0 – 22.5 min 129.1 & 147.1 amu 22.5 – 25.0 min 149.1 & 167.1 amu 25.0 – 26.7 min 149.1 & 279.1 amu
Agilent 6890 Gas Chromatograph with a Agilent 5973 Mass Spectrometer quipped with a Agilent 7683 Autosampler and Agilent Quick Swap Module	

A.1.5.4.2 Sample Collection, Preservation, and Handling

Samples are collected in glass amber bottles and amber glass 40 mL vials with PTFE lined caps. Samples are run within 48 hours of arrival when possible, but if storage is required the samples are stored in the dark at 5°C and analyzed as soon as possible. Record the time in days that the samples were stored.

A.1.5.4.3 Sample Specifications

Care must be taken during sample preparation and handling to reduce environmental phthalate contamination. All glassware should be rinsed with hexanes/chloroform and plastics should be avoided. To enable injection on the GC/MS, the phthalates must be transferred to an organic phase. Therefore, all samples and standards are extracted by liquid liquid extraction.

A.1.5.4.3.1 Liquid Liquid Extraction

All samples and standards are extracted into an organic phase through liquid liquid extraction. Obtain a 20 mL aliquot of sample (or standard), add 0.5 g sodium chloride, and spike in 20 µL of surrogate internal standard. Add 1 mL of chloroform, shake vigorously, and allow layers to separate. After layers have separated shake vigorously again. After attaining separation, transfer 500 µL of the bottom chloroform layer to a GC/MS vial. To the 20 mL sample aliquot that has been extracted with chloroform, add 1 mL of hexanes and repeat the shaking procedure. Once settled, remove 500 µL of the top hexane layer and add to the GC/MS vial with the chloroform aliquot. Add 13 µL of the internal standard and inject on the GC/MS.

A.1.5.4.3.1.1 Calculating the Concentration of the Standards

The concentrations of the analytical standards will be based on the concentration in the water phase (not the concentrated organic phase):

$$C_a = \frac{C_{standard}\, V_{standard}}{V_{Total}}$$

where: C_a = analyte concentration

$C_{Standard}$ = stock phthalate ester concentration

$V_{Standard}$ = volume of phthalate ester standard added to the total volume

V_{Total} = total volume of the sample to be extracted (20mL)

Example: Spiking 100 µL of 100 µg/L DEHA stock standard into 20 mL of reagent water will yield an analytical standard of 0.5 µg/L DEHA. Note that after extraction the concentration in the organic phase injected in the GC/MS is 5 µg/L but the 0.5 µg/L concentration will be used to build the calibration curve.

A.1.5.4.4 Analyte Identification

Prior to each run the elution order of the phthalates will be determined with a standard.

A.1.5.4.5 Instrument Calibration

Each day, prior to the start of a run, the GC/MS will be auto-tuned using the pre-programmed auto-tune function. For quantitation, the relationship between the instrument response and the phthalate concentration should be linear. In addition to the initial calibration curves, the run method includes calibration checks and blanks to verify continued calibration.

A.1.5.4.5.1 Initial Calibration

Calibration standards are run at the start of a run method or every 24 hours. The initial calibration standards consists of the phthalate of interest, IS, and SIS. At least five calibration standards should be prepared with varying phthalate concentrations. The concentrations are chosen such that the sample phthalate concentration lies within the calibration curve. The lowest standard must have a signal-to-noise value (S/N) greater than or equal to 3, while the high concentration should be large enough to cover the desired phthalate range. Each concentration step should double from the prior concentration.

The SIS and IS are spiked into each of the calibration standards: SIS prior to extraction and IS after extraction (just prior to GC injection). The concentration of the IS and SIS must be the same in each calibration standard and sample. The IS and SIS concentration should be higher than that of the lowest calibration standard but not exceed that of the high calibration standard.

A.1.5.4.5.1.1 Calculation of the Signal- to-Noise (S/N) Value

To calculate the S/N Value, calibration standards and control samples are run. Noise is defined as the baseline max to min peak height near the elution time of the analyte. The analyte peak is then defined as the height from the mean noise level to top of peak. The control

sample is the matrix water with no phthalates which is extracted and injected on the GC. From the control sample, the maximum peak height around the elution time of the analyte is determined and ascribed as noise. The peak height for each analyte in the calibration standard is determined and the S/N calculated according to the following equation:

$$\frac{S}{N} = \frac{\left(H_{analyte} - H_{NoiseMean}\right)}{H_{NoiseMax}}$$

where: $H_{analyte}$ = peak height of the analyte in the standard (or sample)

$H_{NoiseMax}$ = maximum peak height in the control right around the elution time of the analyte

$H_{NoiseMean}$ = average peak height of the noise in the control right around the elution time of the analyte

A.1.5.4.5.2 Continuing Calibration

After every 10 samples a check standard is run. The check standard is the mid range calibration standard. A blank is run before and after the standard to be sure carry over is not observed. Acceptance criterion is addressed in 4.5.5.3 (Continuing Calibration Checks).

A.1.5.4.5.3 Blanks

Blanks, consisting of phthalate free HPLC grade hexanes/chloroform (50/50 by volume mix) are included at the start and end of each run, before the check standards, before and after the calibration standards, and after every 10 samples. Placing of blanks throughout the run method identifies carryover or contamination of the system. An example run order is shown in Table A.1.5.4.

A.1.5.4.5.4 Matrix Spikes

Laboratory matrix spikes are used to establish if the sample matrix interferes with the method. A concentrated phthalate stock solution is spiked into a sample prior to liquid liquid extraction. The final phthalate concentration in the spiked sample must not exceed the highest calibration standard. Each run method will have at least one matrix spike. For run methods with 40 or more samples the matrix spikes will be 5% of the total number of samples. For example a run method with 40 samples will have two matrix spikes; while a run method with 60 samples will have 3 matrix spikes.

An example run order that includes initial calibration standards, check standards, blanks, matrix spikes, and samples is shown in Table A.1.5.4. Each initial calibration standard should be run twice.

A.1.5.4.5.5 Relative Response

The relative response (RR) is calculated for the analyte according to the following equation (the same concentration and volume of SIS must be spiked into every sample and standard:

$$RR_a = A_a/A_{SIS}$$

where: A_a = peak area of the analyte

A_{IS} = peak area of the surrogate internal standard

A.1.5.4.5.5.1 Calibration Curve from Relative Response

Calibration curves are constructed from the standards run at the start of each run method. The RR_a is calculated for the analyte and plotted as RR_a versus the known analyte concentration (C_a). From the best fit line, the correlation coefficient (R^2) must be ≥ 0.98 for a 5-point curve. If the criterion for the R^2 is not met, the calibration standards and all samples will be reanalyzed.

A.1.5.4.5.5.2 Relative Response for Phthalate Ester Mixtures

When a sample or standard has multiple phthalates, each peak will be integrated and the RR_a calculated for each analyte. The same criterion as described in section A.1.5.4.5.1.1 applies for each analyte.

A.1.5.4.5.5.3 Continuing Calibration Checks

The continuing calibration checks, run every 10 samples, are considered acceptable if they have less than 25% difference and the blanks run before and after the check standard show no carryover or contamination. The percent difference is calculated as follows:

$$\% \text{ difference} = (C_{aI} - C_a) / C_{aI} \times 100\%$$

where: C_{aI} = Analyte concentration from the initial calibration

C_a = Analyte concentration from continuing calibration check

Table A.1.5.4 Example run order with samples having 100 µg/L phthalate esters

Sample Name	**Description**
Blank1	Hexanes/Chloroform (50/50 by volume)
Control	Extracted Sample – No phthalates
Control	Extracted Sample – No phthalates
25 µg/L standard	Mix of phthalates
25 µg/L standard	Mix of phthalates
50 µg/L standard	Mix of phthalates
50 µg/L standard	Mix of phthalates
100 µg/L standard	Mix of phthalates
100 µg/L standard	Mix of phthalates
200 µg/L standard	Mix of phthalates
200 µg/L standard	Mix of phthalates
400 µg/L standard	Mix of phthalates
400 µg/L standard	Mix of phthalates
Blank2	Hexanes/Chloroform (50/50 by volume)
OP18-YYYY MM DD Matrix Spike	Sample with phthalate addition
Blank3	Hexanes/Chloroform (50/50 by volume)
OP18-01-YYYY MM DD	Sample
OP18-02-YYYY MM DD	Sample
OP18-03-YYYY MM DD	Sample
OP18-04-YYYY MM DD	Sample
**OP18-04-YYYY MM DD **DUP	Instrument duplicate
OP18-05-YYYY MM DD	Sample
OP18-06-YYYY MM DD	Sample
OP18-07-YYYY MM DD	Sample
OP18-08-YYYY MM DD	Sample
**OP18-08-YYYY MM DD **DUP	Instrument duplicate
Blank4	Hexanes/Chloroform (50/50 by volume)
100 µg/L standard	Mix of phthalates
Blank5	Hexanes/Chloroform (50/50 by volume)

Sample Labeling

Operators Initials Experiment Number-Sample Number-Date

OP18-01-YYYY MM DD

OP = Operators initials -01- = Sample Number

18 = Experiment Number YYYY MM DD = Date

A.1.5.4.6 Sample Analysis Procedure

All samples are analyzed under the same GC/MS conditions as for the analytical standards. Sample concentrations must be within the range of the calibration standards used for the calibration curve.

A.1.5.4.6.1 Retention Time

The relative retention time of each analyte will be determined from the initial calibration standards on the day of analysis.

A.1.5.4.6.2 Minimum Peak Height

A signal-to-noise ratio of three is considered a relevant peak. A peak with a signal-to-noise ratio of three or less is considered noise. See section A.1.5.4.5.1.1 for calculation details.

A.1.5.5 Data Analysis

A.1.5.5.1 Data Recording

Appropriate method information and data will be recorded in a laboratory notebook. This notebook will be scanned, saved as a PDF document, and uploaded to the project file on the R drive. Everything analyzed on the GC/MS is logged in the LC/MS instrument notebook. Data calculations and quantification and will be done with *Microsoft Excel*. The chromatograms and *Excel* files are backed up to the R drive and an external hard drive.

A.1.5.5.2 Sample Quantification

The surrogate internal standard linear calibration curve is used to determine the concentrations of phthalates in the samples. The surrogate internal standard, DNHP-D6, is added prior to any extraction and the surrogate internal standard just prior to GC/MS injection. Quantitating with the surrogate internal standard allows for loses or partitioning differences to be accounted for in the calibration curve. The internal standard, PANE-D10, provides information about instrument stability. The quantification of the samples will be done with a linear calibration curve.

A.1.5.5.2.1 Calibration Curve Construction

Using the parameters established in A.1.5.4.5, a calibration curve is constructed such that the y-axis is the relative response (A_A/A_{SIS}) and the x-axis is the initial calibration standards concentration in µg/L (see A.1.5.4.3.1.1).

$$\text{relative response} = (A_A/A_{SIS})$$

where: A_A = peak area of the analyte in the initial calibration standard

A_{SIS} = peak area of the SIS in the initial calibration standard

The equation of the line is calculated using a best fit line for at least 5 data points:

$$y = mx + b$$

where: m = slope and b = y-intercept

A.1.5.5.2.2 Concentration in sample

The relative response is calculated for each analyte in the sample. The concentration is calculated by substituting the relative response into the equation of the line and solving for concentration:

$$\text{Concentration } (\mu g/L) = [(A_{A\_sample}/A_{SIS\_sample}) - b]/\, m$$

where: $A_{A\_samples}$ = peak area of the analyte in the samples

A_{SIS_sample} = peak area of the SIS in the initial calibration standard

A.1.5.5.2.3 Accounting for Liquid/Liquid Extraction

Since the calibration curve is constructed such tha the concentration is based on the concentration in the original sample and not the concentrated sample injected on the instrument no additional calculation is required.

A.1.5.5.3 Multicomponent Analysis

The process described in section A.1.5.5.2 for a single peak can be applied to a chromatogram with multiple peaks. To quantitate multiple peaks: Run analytical standards on GC/MS, use the retention time to confirm the specific analyte, and calculate each analyte peaks as described in A.1.5.5.2.

A.1.5.5.4 Surrogate Internal Standard and Matrix Spike Recovery Calculations

A.1.5.5.4.1 Surrogate Recovery Calculations

Since the IS and SIS are spiked at the same concentration, the following equation is used to calculate the percent recovery of the surrogate from each sample:

$$\% \text{ Recovery} = [A_{SIS} / (\bar{x}RF_{SIS} \times A_{IS})] \times 100$$

where: A_{SIS} = peak area of the surrogate internal standard

A_{IS} = peak area of the internal standard

$\bar{x}RF_{SIS}$ = mean relative response factor of the surrogate internal standard

Variance of greater than 25% in SIS recovery between the standards and samples is considered significant, requiring that the problem be identified and corrected or the samples reanalyzed.

The relative response factor of the SIS is determined from the initial calibration standards:

$$RF_{SIS} = (A_{SIS} \times C_{IS}) / (C_{SIS} \times A_{IS})$$

where: A_{SIS} = peak area of the surrogate internal standard

A_{IS} = peak area of the internal standard

C_{SIS} = concentration of the surrogate internal standard in the initial calibration standard, in micrograms per liter

C_{IS} = concentration of the internal standard in the initial calibration standard, in micrograms per liter

After the RF_{SIS} is calculated for each initial calibration standard, the average is calculated as shown below:

$$\bar{x} = \frac{1}{n} \cdot \sum_{i=1}^{n} x_i$$

where: n = number of initial calibration standards

x_i = the RF_{SIS} value for each initial calibration standard

This average $\bar{x}RF_{SIS}$ value is used in the % recovery equation.

A.1.5.5.4.2 Matrix Spike Recovery

The percent recovery of the matrix spike is calculated according to the following:

$$\% \text{ Matrix Recovery} = (C_{MS} - C_S) / C_{ADD}$$

where: C_{MS} = phthalate concentration in the spiked matrix sample

C_S = phthalate concentration in the original unspiked sample

C_{ADD} = the phthalate concentration that was spiked into the sample

If there is less than 75% recovery another quantitation method, such as standard addition, is required.

A.1.5.6 Quality Control

The specific quality control parameters are described in the following sections:

Instrument calibration standards & rejection parameters	Section A.1.5.4.5.1 to A.1.5.4.5.4
Blanks	Section A.1.5.4.5.3
IS Spike	Section A.1.5.4.5.1
Sample Peak Parameters	Section A.1.5.4.6
Data Recording	Section A.1.5.5.1
Matrix Spike Recovery	Section A.1.5.5.4

A.1.5.7 Safety

Standard laboratory safety practices will be followed including the use of protective clothing and eyeglasses and care when using flammable solvents.

A.1.5.8 Training

Prior to collecting any project-related data, each operator will be trained on the instrumentation and data entry, and will be required to demonstrate capability to obtain data of satisfactory quality.

A.1.6 SOP for Preparing Extraction Water for Fill-and-Dump Tests (Ver. 0.8 with minor edits; 09/14/2012). SOP to be used during fill-and-dump experiment 1 (FD1).

A.1.6.1 Introduction

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, a series of fill-and-dump tests will be conducted using lead and copper pipe sections. This SOP describes the steps needed to prepare the water used for these tests. Preparation of these waters is adapted from NSF/ANSI 61, Appendix B.

A.1.6.2 Definitions

RO water – Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.

Reagent water – Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.

A.1.6.3 Preparation

A.1.6.3.1 Dechlorinated pH 8 Tap Water for Fill-and-Dump Experiments

Water will be collected from a sink in 1116 Learned Hall 24–48 hours prior to each fill-and-dump experiment. The cold water tap will be turned on and flushed for at least five minutes prior to water collection. Water will be collected in a 30 L cylindical Nalgene tank, which will first be rinsed with the tap water before it is filled. Prior to initial use, this tank will be washed with Liquinox soap and water, then rinsed three times each with tap water and RO water and allowed to air-dry. After each use, the remnants will be dumped and the container will be rinsed three times with RO water, allowed to air dry (upside down), and then stored with the lid in place to keep out dust.

Immediately upon filling, samples will be drawn for the following QC purposes: pH, alkalinity, residual chlorine, and TOC. The samples will be promptly analyzed to determine whether the QC objectives described below (see Quality Control) are met. If not, start over or obtain approval from the PI or a co-PI to proceed. After checking the residual chlorine

concentration, dechlorinate the water, but do not adjust the pH of the water until immediately prior to use.

Immediately prior to use, samples of this water will be drawn for the following analyses: pH, conductivity, metal ions (lead, copper, antimony when appropriate, sodium and potassium, and other metals by ICP when desired), alkalinity, water hardness, anions, organic compounds, and TOC. Collect at least triplicate samples for TOC analysis. All measurements will be carried out following the appropriate SOPs.

Dechlorination: Dechlorinate the tap water by drop-wise addition of a 17 g/L solution of sodium sulfite (1.7 g Na_2SO_3 per 100 mL) or a 14.6 g/L solution of sodium bisulfite (1.46 g $NaHSO_3$ per 100 mL). One drop of each solution should remove ~ 0.5 mg of residual chlorine. Begin by adding the amount needed to stoichiometrically remove the residual chlorine, test for residual chlorine, then add more as needed until a test for total residual chlorine demonstrates the absence of a chlorine residual. Do not add excess dechlorinating agent beyond that needed to dechlorinate the water, as this will affect the dissolved oxygen level. Test for residual chlorine using any convenient method: a Hach TCR ampule, DPD solution with buffer and iodide added, or amperometric titration. Mix the dechlorinating agent into the water by stirring it with a short (2 ft.) length of clean 3/4-in. (nom.) HDPE tubing.

pH adjustment: The water will be adjusted to pH 8.0 immediately before use using 0.10 N HCl and NaOH solutions, as needed. The sodium hydroxide solution will be a 0.10 N solution prepared by adding 4.0 g of reagent grade sodium hydroxide to reagent water. The hydrochloric acid solution will be a 0.10 N solution prepared by adding trace-metal grade concentrated hydrochloric acid to reagent water. The pH of the water will be adjusted in the Nalgene tank with gentle stirring. The pH of the solution will be monitored during adjustment using a Fisher AB15 benchtop pH meter or Accumet XL25 pH meter. Consider the pH adjustment complete when the water remains at pH 8.0 $\pm$ 0.1 units for 2 minutes following the last acid or base addition. Use a short length of clean 3/4-in. (nom.) HDPE tubing to stir the water in the reservoir.

A.1.6.3.2 Low-pH extraction water

A pH 6.5 extraction water ("low pH water") will be prepared for metal leaching experiments (and also to examine the effect of pH on leaching of organic contaminants). This water will be prepared and stored in glass containers. Brand-new previously unused containers, containers previously used only to hold LC/MS water, or containers cleaned in a trace-metal acid bath, as described in the SOP for lead analysis, will be used to prepare and store this water. The water will consist of reagent water spiked with 25 mL/L of 0.04 M $NaHCO_3$ and 25 mL/L of 0.04 M $CaCl_2$ per liter of water (per NSF International) and adjusted to pH 6.5 $\pm$ 0.2 units using 0.1 N HCl (and no more than 5 drops of 0.1 N NaOH in the event that a slight excess of HCl is inadvertently added). All solutions will be prepared using reagent-grade chemicals. The pH of this water will be adjusted immediately prior to use in fill-and-dump experiments to minimize exchange of CO_2 with the atmosphere and the resulting change in pH. The container will be kept capped to minimize loss of CO_2.

Immediately prior to use, samples of this water will be drawn for the following analyses: metal ions (lead, copper, antimony when appropriate, and other metals by ICP when desired), organic compounds, and TOC. Collect at least triplicate samples for TOC analysis. All measurements will be carried out following the appropriate SOPs.

A.1.6.3.3 Chlorinated pH 8 extraction water

Chlorinated pH 8 extraction water will be prepared to examine the effects of a free chlorine residual on leaching of organic compound and formation of chlorinated byproducts. This water will be prepared and stored in glass containers. Brand-new previously unused containers, containers previously used only to hold LC/MS water, or containers cleaned in a trace-metal acid bath, as described in the SOP for lead analysis, will be used to prepare and store this water. The water will consist of reagent water spiked with 25 mL/L of 0.04 M $NaHCO_3$ and 25 mL/L of 0.04 M $CaCl_2$ per liter of water (per NSF International).

This water may be prepared in advance, but the chlorine should be added and the pH adjusted immediately prior to use – to avoid decay of the chlorine residual and to minimize loss of CO2 (and the need for additional pH adjustment).

Chlorinate the water immediately prior to use by adding the amount of laboratory-grade sodium hypochlorite solution (Fisher Chemical Cat#:SS290-1; 5.65–6%), diluted first if necessary, to produce a free chlorine residual of 2.0 $\pm$ 0.2 mg/L. Confirm that the chlorine residual is free (not combined) and immediately before using this water determine the free chlorine residual using the Hach ampule method. The chlorine solution is to be stored in the dark in a refrigerator.

After adding chlorine and immediately prior to use, adjust the pH of this water to pH 8.0 $\pm$ 0.1 units using 0.1 N HCl and 0.1 N NaOH. Keep the container capped to minimize loss of CO_2. Immediately prior to use, samples of this water will be drawn for the following analyses: metal ions (lead, copper, antimony when appropriate, and other metals by ICP when desired), organic compounds, TOX, and TOC. Collect at least triplicate samples for TOC analysis. All measurements will be carried out following the appropriate SOPs.

A.1.6.4 Reporting

Each batch of water will be uniquely labeled and all measured properties of that batch will be recorded in student notebooks at the time of preparation. This information will be identified with the set of experiments the water is used in for all subsequent data analysis and interpretation. Each batch will be designated in the format XX-YY-Date, where XX will be DT for dechlorinated tap water; LP for low pH water; and CL for chlorinated water, YY will refer to the incremental number of the batch, and Date is the date the water was prepared.

A.1.6.5 Quality Control

Extraction water properties will be analyzed the same day the water is prepared to ensure that the water is within the correct range for the fill-and-dump experiments. All quality control measures for the individual analyses will be conducted in accordance with the specific SOPs for that analysis. The tap water must initially have a pH (before adjustment) of 7–10, an alkalinity of 40–100 mg/L as $CaCO_3$, a combined chlorine residual of 2–4 mg/L, and a TOC concentration $\leq$ 10 mg/L (measured using either the high-temperature combustion method or UV-persulfate method). If the water does not meet these specifications, it may only be used after direct authorization by the PI or a co-PI. Otherwise, the water should be discarded, and a new batch prepared.

Samples of each batch of extraction water will be collected immediately prior to the fill-and-dump experiments and analyzed for concentrations of water hardness, dissolved metals and organic compounds. These will be considered to be background concentrations of each analyte for the fill-and-dump experiments. Additional aliquots of this water will be collected for use as laboratory fortified matrix blanks in the metal and organic analysis procedures, as outlined in the SOPs for the individual analytes

A.1.7 SOP for Preparing Extraction Water for Fill-and-Dump Tests (Ver. 2.0 with minor edits; 04/20/2013). SOP to be used during fill-and-dump experiments 2 and 3 (FD2 and FD3).

A.1.7.1 Introduction

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, a series of fill-and-dump tests will be conducted using lead and copper pipe sections. This SOP describes the steps needed to prepare the water used for these tests. Preparation of these waters is adapted from NSF/ANSI 61, Appendix B.

A.1.7.2 Definitions

RO water – Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.

Reagent water – Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.

A.1.7.3 Preparation

A.1.7.3.1 Dechlorinated pH 8 tap water (DT)

Water will be collected from a sink in 1116 Learned Hall 24–48 hours prior to each fill-and-dump experiment. The cold water tap will be turned on and flushed for at least five minutes prior to water collection. Water will be collected in a 30 L cylindrical Nalgene tank, which will first be rinsed with the tap water before it is filled. Prior to initial use, this tank will be washed with Liquinox soap and water, then rinsed three times each with tap water and RO water and allowed to air-dry. After each use, the remnants will be dumped and the container will be rinsed three times with RO water, allowed to air dry (upside down), and then stored with the lid in place to keep out dust.

Immediately upon filling, samples will be drawn for the following QC purposes: pH, alkalinity, residual chlorine, and TOC. The samples will be promptly analyzed to determine whether the QC objectives described below (see Quality Control) are met. If not, start over or obtain approval from the PI or a co-PI to proceed. After checking the residual chlorine

concentration, dechlorinate the water, adjust the pH of the water; then check and adjust the pH of the water again immediately prior to use.

Immediately prior to use, samples of this water will be drawn for the following analyses: pH, conductivity, metal ions (lead, copper, antimony when appropriate, sodium and potassium, and other metals by ICP when desired), alkalinity, water hardness, anions, organic compounds, and TOC. Collect at least triplicate samples for TOC analysis. All measurements will be carried out following the appropriate SOPs.

Dechlorination: Dechlorinate the tap water by drop-wise addition of a 17 g/L solution of sodium sulfite (1.7 g Na_2SO_3 per 100 mL) or a 14.6 g/L solution of sodium bisulfite (1.46 g $NaHSO_3$ per 100 mL). One drop of each solution should remove ~ 0.5 mg of residual chlorine. Begin by adding the amount needed to stoichiometrically remove the residual chlorine, test for residual chlorine, then add more as needed until a test for total residual chlorine demonstrates the absence of a chlorine residual. Do not add excess dechlorinating agent beyond that needed to dechlorinate the water, as this will affect the dissolved oxygen level. Test for residual chlorine using any convenient method: a Hach TCR ampule, DPD solution with buffer and iodide added, or amperometric titration. Mix the dechlorinating agent into the water by stirring it with a short (2 ft.) length of clean 3/4-in. (nom.) HDPE tubing.

pH adjustment: The water will be adjusted to pH 8.0 using 0.10 N HCl and NaOH solutions, as needed. The sodium hydroxide solution will be a 0.10 N solution prepared by adding 4.0 g of reagent grade sodium hydroxide to reagent water. The hydrochloric acid solution will be a 0.10 N solution prepared by adding trace-metal grade concentrated hydrochloric acid to reagent water. The pH of the water will be adjusted in the Nalgene tank with gentle stirring. The pH of the solution will be monitored during adjustment using a Fisher AB15 benchtop pH meter or Accumet XL25 pH meter. Consider the pH adjustment complete when the water remains at pH 8.0 + 0.1 units for 2 minutes following the last acid or base addition; however, the pH of the water will rise upon standing (due to loss of CO2), so it will need to be adjusted again immediately prior to use. Use a short length of clean 3/4-in. (nom.) HDPE tubing to stir the water in the reservoir.

A.1.7.3.2 Chlorinated pH 8 extraction water (Cl)

Chlorinated pH 8 extraction water will be prepared to examine the effects of a free chlorine residual on leaching of organic compound and formation of chlorinated byproducts. This water will be prepared and stored in glass containers. Brand-new previously unused containers, containers previously used only to hold LC/MS water, or containers cleaned in a trace-metal acid bath, as described in the SOP for lead analysis, will be used to prepare and store this water. The water will consist of reagent water spiked with： 0.56 mM $NaHCO_3$, 1 mM $CaCl_2$, and 0.44 mM NaCl (14.0 mL of 0.04 M $NaHCO_3$, 25 mL of 0.04 M $CaCl_2$,and 11.0 mL of 0.04 M NaCl per liter of extraction water). This water is similar in composition to the pH 8 extraction water specified by NSF International, but is close to equilibrium with the atmosphere with respect to CO_2, so the pH will not change much as it is poured into and out of the pipe specimens. Immediately prior to use, check the pH and, if necessary, adjust it 8.0 using 0.1 N HCl or NaOH.

This water may be prepared in advance, but the chlorine should be added immediately prior to use – to avoid decay of the chlorine residual. Chlorinate the water immediately prior to use by adding the amount of laboratory-grade sodium hypochlorite solution (Fisher Chemical Cat#:SS290-1; 5.65–6%), diluted first if necessary, to produce a free chlorine residual of 2.0 ± 0.2 mg/L. Confirm that the chlorine residual is free (not combined) and immediately before using this water determine the free chlorine residual using the Hach ampule method. The chlorine solution is to be stored in the dark in a refrigerator.

Keep the container capped to minimize contamination. Immediately prior to use, samples of this water will be drawn for the following analyses: metal ions (lead, copper, antimony when appropriate, and other metals by ICP when desired), organic compounds, TOX, and TOC. Collect at least triplicate samples for TOC analysis. All measurements will be carried out following the appropriate SOPs.

A.1.7.3.3 Low-pH extraction water (LP)

A pH 6.5 extraction water (“low pH water”) will be prepared for metal leaching experiments (and also to examine the effect of pH on leaching of organic contaminants). This water will be prepared and stored in glass containers. Brand-new previously unused containers,

containers previously used only to hold LC/MS water, or containers cleaned in a trace-metal acid bath, as described in the SOP for lead analysis, will be used to prepare and store this water. The water will consist of reagent water spiked with 0.018 mM $NaHCO_3$, 1 mM $CaCl_2$, and 0.982 mM NaCl (0.45 mL of 0.04 M $NaHCO_3$, 25 mL of 0.04 M $CaCl_2$,and 24.55 mL of 0.04 M NaCl per liter of extraction water). This water is similar in composition to the pH 6.5 extraction water specified by NSF International, but is close to equilibrium with the atmosphere with respect to CO_2, so the pH will not change much as it is poured into and out of the pipe specimens. Immediately prior to use, check the pH and, if necessary, adjust it to pH 6.5 $\pm$ 0.2 units using 0.1 N HCl (and no more than 5 drops of 0.1 N NaOH in the event that a slight excess of HCl is inadvertently added). All solutions will be prepared using reagent-grade chemicals. The container will be kept capped to minimize the potential for contamination.

Immediately prior to use, samples of this water will be drawn for the following analyses: metal ions (lead, copper, antimony when appropriate, and other metals by ICP when desired), organic compounds, and TOC. Collect at least triplicate samples for TOC analysis. All measurements will be carried out following the appropriate SOPs.

A.1.7.4 Reporting

Each batch of water will be uniquely labeled and all measured properties of that batch will be recorded in student notebooks at the time of preparation. This information will be identified with the set of experiments the water is used in for all subsequent data analysis and interpretation. Each batch will be designated in the format XX-YY-Date, where XX will be DT for dechlorinated tap water; LP for low pH water; and CL for chlorinated water, YY will refer to the incremental number of the batch, and Date is the date the water was prepared.

A.1.7.5 Quality Control

Extraction water properties will be analyzed the same day the water is prepared to ensure that the water is within the correct range for the fill-and-dump experiments. All quality control measures for the individual analyses will be conducted in accordance with the specific SOPs for that analysis. The tap water must initially have a pH (before adjustment) of 7–10, an alkalinity of 40–100 mg/L as $CaCO_3$, a combined chlorine residual of 2–4 mg/L, and a TOC concentration $\leq$ 10 mg/L (measured using either the high-temperature combustion method or

UV-persulfate method). If the water does not meet these specifications, it may only be used after direct authorization by the PI or a co-PI. Otherwise, the water should be discarded, and a new batch prepared.

Samples of each batch of extraction water will be collected immediately prior to the fill-and-dump experiments and analyzed for concentrations of water hardness, dissolved metals and organic compounds. These will be considered to be background concentrations of each analyte for the fill-and-dump experiments. Additional aliquots of this water will be collected for use as laboratory fortified matrix blanks in the metal and organic analysis procedures, as outlined in the SOPs for the individual analytes.

A.1.8 SOP for Conducting Fill-and-Dump Tests with an Epoxy Coating (Ver. 1; 09/15/2012).

SOP to be used during fill-and-dump experiment 1 (FD1).

A.1.8.1 Introduction

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, a series of fill-and-dump tests will be conducted using lined or coated lead and copper pipe sections (and unlined or uncoated control sections). This SOP describes the steps taken to conduct these tests. This method references other SOPs on the preparation of extraction water and on the measurement of individual water constituents.

A.1.8.2 Definitions

RO water – Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.

Reagent water – Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.

Extraction waters (described in the SOP for extraction water preparation): 1) dechlorinated tap water adjusted to pH 8.0; 2) chlorinated pH 8 extraction water containing 1 mM $NaHCO_3$ and 1 mM $CaCl_2$ and having a free chlorine concentration of about 2 mg/L; and 3) low pH extraction water having a pH of 6.5 – a more aggressive water used especially to test pipe samples for metal leaching and also for leaching of organic compounds at a lower pH value.

A.1.8.3 Materials

A.1.8.3.1 Pipe Samples

Pipe samples obtained from participating utilities and subsequently lined or coated, except for the unlined / uncoated control samples. The linings and coatings will be installed / applied by representatives of the manufacturers when possible, following their own procedures, so that the lining or coating will conform to the manufacturer's specifications. For epoxy coating, this includes sandblasting the interior of the pipes to remove surface materials, followed by the application of the coating and overnight curing. The pipes will then be shipped back to the

University of Kansas by overnight delivery. Upon receipt of the pipe samples at KU, they will be examined for damage to the pipe or the end-fittings. Pipes with significant damage may be removed from the experiment at this time. To minimize any additional curing time, fill-and-dump experiments will begin immediately after the coated or lined pipe samples are received. If enough samples are available, however, some of the coated pipe samples may be set aside for later experiments. For all tests, a control sample consisting of an unlined and uncoated pipe will also be used. This control sample will remain at KU throughout the coating or lining process, to reduce shipping costs and to better maintain the control section in its native state, i.e., so that the results of the lined and coated pipe sections can be compared to those from a relatively undisturbed pipe section and not to one that has been sand-blasted, scraped, or otherwise prepared for lining or coating.

A.1.8.3.2 Extraction Waters

Batches of extraction water (dechlorinated tap water, chlorinated pH 8 extraction water, and low-pH extraction water) will be prepared in advance of the fill-and-dump tests following the procedures outlined in the SOP for Preparing Extraction Water for Fill-and-Dump Tests. These waters will be allowed to reach room temperature prior to use in the fill-and-dump experiments. Samples of the dechlorinated tap water will be collected and analyzed for pH, dissolved oxygen, conductivity, alkalinity, and total chlorine prior to use. Additional samples of dechlorinated tap water will be collected and stored for analysis of total hardness, major anions, TOC, lead, copper, and any other relevant metals, as these analyses may be conducted after the fill-and-dump experiments have been carried out. Samples of the chlorinated pH 8 extraction water and the low-pH extraction water will be collected for analysis of all analytes to be determined on extracts. All sample collection, storage, and analysis procedures will be conducted following the relevant SOPs.

A.1.8.4 Experimental Procedure

A.1.8.4.1 Preparation

After the pipe samples are inspected (as described above), the pipe nipples on each end should be thoroughly rinsed with tap water and wiped with a clean laboratory towel (WypAll X60) to remove any loose residues potentially containing lead.

Pipe samples will be flushed with cold tap water for 15 minutes to remove any particles or other debris from the interior of the pipe surfaces. The exact flushing time actually used will be recorded, and should be consistent among individual pipe samples within each fill-and-dump experiment. The pipe samples may be flushed individually or connected in series, but the control pipe samples (having potentially high lead or copper levels) should occupy the last position when placed in series. When connecting pipe samples to the flushing manifold, handle them carefully to avoid damaging the lining or coating. Be especially careful not to twist the pipe nipples, which could create a gap in the lining or coating and expose Pb or Cu metal to the extraction water. Hand tighten all connections if possible. If a wrench is needed to stop a leak, use two wrenches – one to hold the pipe nipples stationary and the other to tighten the fitting.

The flushing water will be discharged directly into the sink, and will not be retained for analysis. Following flushing, each pipe sample will be rinsed with 50-100 mL of the desired extraction water and then filled with that same water. The pipe sample will then be sealed with silicone stoppers, and the date and time recorded as the start time for the fill-and-dump experiment for that pipe section.

A.1.8.4.2 Design of the Test Matrix

Fill-and-dump tests will be conducted for different lengths of time on different pipe sections to determine the impact of contact time on leaching of metal and organic compounds. The specific schedule for each set of tests will be determined prior to beginning the fill-and-dump experiment and will depend on the total number of pipe samples available. In each case, similar experiments will be carried out using dechlorinated tap water and chlorinated extraction water. At least one test condition will be carried out in duplicate to examine the reproducibility of our results. For the first set of experiments, we anticipate having at least seven coated pipe

sections available for both the lead and copper pipes, along with one control pipe of each material. The full test matrix for this experiment is shown below. This matrix will be applied to both the lead and copper pipe sections, with the fill-and-dump experiments for each type of pipe being conducted simultaneously.

Table A.1.8.1 Holding times and fill solutions for lead and copper pipe sections

	Dechlorinated Tap Water		Chlorinated Water
Holding Time	# of Coated Sections	# of Control Sections	# of Coated Sections
6 hours	2	1	1
24 hours	1	--	1
4 days	1	--	1

A.1.8.4.3 Collection of Water for Analysis

At the end of the designated reaction time for each pipe section, one end of the pipe section will be unsealed. The water within that pipe section will then be poured into a glass beaker that has been pre-cleaned and drip-dried. The pre-cleaning method will consist of 1) rinsing with methanol to remove any organic compounds; 2) rinsing with RO water; 3) immersion in an HCl acid bath for 2–24 hours; 4) rinsing with RO water; and 5) rinsing with reagent water. Beakers that are reused from one test to another will be cleaned in the same manner. Due to the anticipated high levels of lead or copper (and possible lead or copper particles) in the control pipe sections, special beakers will be designated for use with the control pipe sections only. These beakers will be cleaned between uses using Liquinox detergent and water to remove particles, then rinsed in the same manner as the other beakers.

A.1.8.4.3.1 Sections with dechlorinated tap water

Once in the beaker, sub-samples of this water will then be poured out and collected for analysis as follows:

Table A.1.8.2 Analysis of dechlorinated tap water from pipe sections

Method	**Volume**	**Storage**	**Notes**
pH	20 mL	50 mL beaker	Analyze immediately
Lead and Copper	10 mL	PE test tube	Preserve with nitric acid
Metals by ICP	20 mL	PE test tube	Preserve with nitric acid
Total Organic Carbon	40 mL*	EPA vial	Preserve with H_3PO_4 to pH ~ 2

*If limited volume available, collect only 30 mL

The remaining sample will be transferred to a glass bottle for analysis of organic compounds. An additional 10 mL sample will be collected from the control pipe and stored for lead and copper analysis in case a filtered sample is needed for dissolved metals. Excess sample beyond that needed for organic analysis will be used to obtain backup samples for other tests as needed.

A.1.8.4.3.2 Sections with chlorinated pH 8 extraction water

Once in the beaker, sub-samples of this water will then be poured out and collected for analysis as follows:

Table A.1.8.3 Analysis of chlorinated pH 8 extraction water from pipe sections

Method	Volume	Storage	Notes
pH	20 mL	50 mL beaker	Analyze immediately
Lead and Copper	10 mL	PE test tube	Preserve with nitric acid
Metals by ICP	20 mL	PE test tube	Preserve with nitric acid
Total Organic Carbon	40 mL*	EPA vial	Preserve with H_3PO_4 to pH ~2
Free chlorine	50 mL	150-mL beaker	Analyze immediately
TOX	50 mL	50-mL serum bottle	Dechlorinate, then preserve with HNO_3 to pH ≤ 2†

*If limited volume available, collect only 20-30 mL

† Dechlorinate by adding 1-2 drops of one of the dechlorinating solutions described in the SOP for preparing extraction waters, and preserve by adding 3 drops of concentrated HNO_3 per 50–60 mL sample.

The remaining sample will be transferred to a glass bottle, for analysis of organic compounds, and will be immediately dechlorinated by adding, to each 100 mL of sample, 2 drops of a 1/10th dilution of one of the dechlorinating solutions described in the SOP for preparing extraction waters. Check immediately to verify that the residual chlorine has been quenched; if not, add additional 1/10th-strength dechlorinating solution dropwise until the sample is dechlorinated. Excess sample beyond that needed for organics analysis will be used as backup samples for other tests as needed. If less than 230 mL is initially present in the beaker, the volumes collected for total organic carbon and metals by ICP analysis will be reduced to provide sufficient volume (at least 50 mL) for organics analysis.

A.1.8.4.4 Metal Leaching Tests

Leaching tests with the low-pH (6.5) extraction water will be conducted on two pipe sections of each type following the initial fill-and-dump tests. For both lead and copper pipes, one of the pipe samples filled with dechlorinated tap water for 6 hours and one filled with chlorinated pH 8 extraction water will be used for these tests, as well as the control (uncoated) pipe section. This test will begin the day after the six hour fill-and-dump tests are completed. The pipe sections will be flushed with 100 mL of pH 6.5 water to remove any water from the initial fill-and-dump tests. Then each pipe section will be filled with pH 6.5 water and sealed. After six hours, the water will be poured from the pipe into a glass beaker. Sub-samples of the water will be collected for analysis as described above for sections containing dechlorinated tap water.

Following the 6-hour fill-and-dump test with pH 6.5 water, the same pipe sections will be restoppered and stored up to 48 hours before starting a long-term metals leaching test. They will then be rinsed with 100 mL RO water, rinsed with 100 mL of pH 6.5 water, filled with pH 6.5 water, resealed, and held for one week. At the end of that time, the sections will be emptied and subsamples collected for analysis in the same manner described above for sections containing dechlorinated tap water.

A.1.8.4.5 Long-Term Organic Leaching Tests

Upon completion of the 24 hour fill-and-dump tests, the same pipe sections will be rinsed with 100 mL of either dechlorinated tap water or chlorinated extraction water (whichever they previously contained), refilled with the same water and sealed. These sections will be left for 10 days. At the end of that time, the sections will be emptied and subsamples collected for analysis in the appropriate manner for the specific water as described above.

A.1.8.4.6 Storage of Pipe Sections After Use

Pipe sections not being reused within 48 hours will be drained and allowed to dry before being resealed with vinyl end caps. Pipe sections being reused within 48 hours for additional testing (including the metal leaching tests and long-term organic leaching tests described

above) will be drained and stored while still damp by sealing the ends with clean stoppers or vinyl end caps.

A.1.8.4.7 Room Temperature

Record the room temperature in your lab notebook at least twice each day (a.m. and p.m.) when tests are in progress. If the room temperature drop below 20 °C or rises above 25 °C, attempt to remedy the problem (e.g., by adjusting the thermostat or opening a door or window) and notify the PI or a co-PI.

A.1.8.5 Reporting and Labeling

Each coated or lined pipe section, as well as all control sections used in the fill-and-dump experiments, will be assigned a unique identifier. This identifier will consist of the letter L or C (for lead and copper pipes, respectively) and a number. This number will increment from L0 (the lead pipe control section) and C0 (the copper pipe control section) and will not be reused. For each section the date of initial coating will be recorded, as well as the dates and nature (type of water, length of time) for any fill-and-dump experiments that pipe participated in. These data will be recorded in a spreadsheet to allow for tracking of the full experimental history of each pipe section. Any additional observations on the pipe section (damage, corrosion, etc.) will be noted in the same spreadsheet.

Each fill-and-dump experiment will be assigned an experiment number that will be recorded in the laboratory notebook. Experiment numbers for fill-and-dump experiments will be of the format FD-YY-Date, where FD refers to a fill-and-dump experiment, YY is the incremental number of the experiment and Date is the start date of the experiment. All aqueous samples collected during the fill-and-dump experiments will be labeled with the experiment number followed by the sample identification (ID) number. Sample ID numbers will be recorded in the laboratory notebook along with a full description of the sample. These sample ID numbers will also be used in any electronic files produced during analysis of the sample.

A.1.9 SOP for Conducting Follow-up Fill-and-Dump Tests with an Epoxy Coating FD-2 (5/2/13)

A.1.9.1 Introduction

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, a series of fill-and-dump tests will be conducted using lined or coated lead and copper pipe sections (and unlined or uncoated control sections). This SOP describes the steps taken to conduct one subset of these tests, i.e., FD-02, a follow up to the first test (FD-01) conducted using epoxy-lined pipe sections. This method references other SOPs on the preparation of extraction water and on the measurement of individual water constituents.

A.1.9.2 Definitions

RO water – Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.

Reagent water – Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.

Extraction water (described in the SOP for Preparing Extraction Water for Fill-and-Dump Tests, Ver. 2.0): chlorinated pH 8 extraction water (CL) containing 0.56 mM $NaHCO_3$, 1 mM $CaCl_2$, and 0.44 mM NaCl and having a free chlorine concentration of about 2 mg/L.

A.1.9.3 Materials

A.1.9.3.1 Pipe Samples

Selected pipe sections used in fill-and-dump experiment FD-01, plus two previously unused pipe sections, will be used in this experiment (FD-02).

A.1.9.3.2 Extraction Water

Batches of extraction water (chlorinated pH 8 extraction water) will be prepared in advance of the fill-and-dump tests following the procedures outlined in the SOP for Preparing Extraction Water for Fill-and-Dump Tests, Ver. 2.0. The water will be allowed to reach room temperature prior to use in the fill-and-dump experiments. Samples of the chlorinated pH 8 extraction water (CL) will be collected for analysis of all analytes to be determined on extracts.

All sample collection, storage, and analysis procedures will be conducted following the relevant SOPs.

A.1.9.4 Experimental Procedure

A.1.9.4.1 Preparation

The two previously unused pipe sections will be flushed with cold tap water for 15 minutes to remove any particles or other debris from the interior of the pipe surfaces. When connecting pipe samples to the flushing manifold, handle them carefully to avoid damaging the lining or coating. Be especially careful not to twist the pipe nipples, which could create a gap in the lining or coating and expose Pb or Cu metal to the extraction water. Hand tighten all connections if possible. If a wrench is needed to stop a leak, use two wrenches – one to hold the pipe nipples stationary and the other to tighten the fitting. The flushing water will be discharged directly into the sink, and will not be retained for analysis.

Each pipe sample will be rinsed with 100 mL of extraction water and then filled with extraction water. The pipe sample will then be sealed with silicone stoppers, and the date and time recorded as the start time for the fill-and-dump experiment for that pipe section.

A.1.9.4.2 Design of the Test Matrix

Fill-and-dump tests will be conducted for different lengths of time on different pipe sections to determine the impact of contact time on leaching of metals and organic compounds and on chlorine demand. The specific schedule for the tests is shown below (Table A.1.9.1). This matrix will be applied to both the lead and copper pipe sections, with the fill-and-dump experiments for each type of pipe being conducted simultaneously.

A separate test will be performed to determine the short-term chlorine demand of two pipe sections and changes over time. Two pipes (Pb5806 and Cu1206) will be filled with chlorinated pH 8 extraction water. After one hour, samples will be collected and immediately tested to determine the amount of free chlorine remaining. These tests will be repeated until either: 1) remaining free chlorine concentration is constant for at least three consecutive tests or 2) free chlorine demand is no longer observed.

Table A.1.9.1 Relevant pipe information for FD-02

Pipe	Relevant FD-01 Info	Analytes	Detention Time
Pb5802	Stored wet with Milli-Q	All – see below	24 h, then 7 d
Cu1202	Stored wet with Milli-Q, High TOC (4.78)	All – see below	24 h, then 7 d
Pb5805	High Pb (3.8, then 0.8)	All – see below	24 h, then 7 d
Cu1205	Detectable level of Pb (0.7)	All – see below	24 h, then 7 d
Pb5804	Control, never exposed to CL	All – see below	24 h, then 7 d
Cu1210	Control, never exposed to CL	All – see below	24 h, then 7 d
Pb5809	Unused (needs flushed)	All – see below	24 h, then 7 d
Cu5809	Unused (needs flushed)	All – see below	24 h, then 7 d
Pb5808	Exposed only to CL extraction water, High TOC (13.1)	All – see below	6 h
Cu1208	Exposed only to CL extraction water	All – see below	6 h
Pb5806	Exposed only to CL extraction water	Cl_2 Demand & pH Only	1 h, 1 h, …
Cu1206	Exposed only to CL extraction water	Cl_2 Demand & pH Only	1 h, 1 h, …

A.1.9.4.3 Collection of Water for Analysis

At the end of the designated reaction time for each pipe section, one end of the pipe section will be unsealed. The water within that pipe section will then be poured into a glass beaker that has been pre-cleaned and drip-dried. The pre-cleaning method will consist of 1) rinsing with methanol to remove any organic compounds; 2) rinsing with RO water; 3) immersion in an HCl acid bath for 2–24 hours; 4) rinsing with RO water; and 5) rinsing with reagent water. Beakers that are reused from one test to another will be cleaned in the same manner. Due to the anticipated high levels of lead or copper (and possible lead or copper particles) in the control pipe sections (Pb5804 and Cu1210), special beakers will be designated for use with the control pipe sections only. These beakers will be cleaned between uses using Liquinox detergent and water to remove particles, then rinsed in the same manner as the other beakers.

Once in the beaker, sub-samples of this water will then be poured out and collected for analysis as follows:

Table A.1.9.2 Samples Volumes and Analysis for FD-02

Method	Volume	Storage	Notes
pH	20 mL	50 mL beaker	Analyze immediately
Lead and Copper	10 mL	PE test tube	Preserve with nitric acid
Metals by ICP	20 mL	PE test tube	Preserve with nitric acid
Total Organic Carbon	40 mL*	EPA vial	Preserve with H_3PO_4 to pH ~2
Free chlorine	50 mL	150-mL beaker	Analyze immediately

*If limited volume available, collect only 20-30 mL

The remaining sample will be transferred to a 4-oz. glass bottle, for analysis of organic compounds, and will be immediately dechlorinated by adding, to each 100 mL of sample, 2 drops of a 1/10th dilution of one of the dechlorinating solutions described in the SOP for preparing extraction waters. Check immediately to verify that the residual chlorine has been quenched; if not, add additional 1/10th-strength dechlorinating solution dropwise until the sample is dechlorinated. Excess sample beyond that needed for organics analysis will be used as backup samples for other tests as needed.

Samples for analysis of organic compounds will not be collected from the uncoated control pipe sections (Pb5804 and Cu1210) or from those used in the short-term Cl_2 demand tests (Pb5806 and Cl1206). Samples from the latter sections will be analyzed only for Cl_2 and pH.

A.1.9.4.4 Re-flushing and Re-extraction of Selected Pipe Sections

Upon completion of the tests described above, eight pipe specimens (Pb02, Cu02, Pb05, Cu05, Pb08, Cu08, Pb09, and Cu09 were re-flushed for 15 min. with tap water (chloraminated), then rinsed with 100 mL of chlorinated pH 8 reagent water, then refilled and left standing for 6 h, 24 h, and 7 days.

A.1.9.4.5 Storage of Pipe Sections After Use

Once tests are completed on a pipe section, it will be stored in the same manner (wet or dry) as it was previously stored. Those stored dry will be drained and allowed to dry before

being resealed with vinyl end caps. Those stored wet will be filled with reagent water and capped with silicone stoppers, then refilled again with reagent water every 7 days.

A.1.9.4.6 Room Temperature

Record the room temperature in your lab notebook at least twice each day (a.m. and p.m.) when tests are in progress. If the room temperature drop below 20 °C or rises above 25 °C, attempt to remedy the problem (e.g., by adjusting the thermostat or opening a door or window) and notify the PI or a co-PI.

A.1.9.5 Reporting and Labeling

Each sample will be assigned a unique identifier. This identifier will consist of the letters Pb or Cu (for lead and copper pipes, respectively) followed by the last two letters of the pipe section number and the extraction water retention time. For example, the sample collected from pipe section Pb5802 after 24 hours will be labeled Pb02-24.

For each section the date of initial coating and its use in previous experiments has been recorded. The relevant information from this experiment will be added to the existing data base to allow for tracking of the full experimental history of each pipe section. Any additional observations on pipe sections (damage, corrosion, etc.) will be noted in the same spreadsheet.

Each fill-and-dump experiment will be assigned an experiment number that will be recorded in the laboratory notebook. Experiment numbers for fill-and-dump experiments will be of the format FD-YY-Date, where FD refers to a fill-and-dump experiment, YY is the incremental number of the experiment and Date is the start date of the experiment. All aqueous samples collected during the fill-and-dump experiments will be labeled with the experiment number followed by the sample identification (ID) number. Sample ID numbers will be recorded in the laboratory notebook along with a full description of the sample. These sample ID numbers will also be used in any electronic files produced during analysis of the sample.

A.1.10 SOP for Conducting Fill-and-Dump Tests with a PET Lined Specimens, FD-03 (05/31/13; Rev 2.0)

A.1.10.1 Introduction

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, a series of fill-and-dump tests will be conducted using lined or coated lead and copper pipe sections (and unlined or uncoated control sections). This SOP describes the steps taken to conduct the tests done using PET-lined pipe specimens. This method references other SOPs on the preparation of extraction water and on the measurement of individual water constituents.

A.1.10.2 Definitions

RO water – Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.

Reagent water – Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.

Extraction waters (described in the SOP for extraction water preparation): 1) dechlorinated tap water adjusted to pH 8.0; 2) chlorinated pH 8 extraction water containing 0.56 mM $NaHCO_3$, 1 mM $CaCl_2$, and 0.44 mM NaCl and having a free chlorine concentration of about 2 mg/L; and 3) low pH extraction water containing 0.018 mM $NaHCO_3$, 1 mM $CaCl_2$, and 0.912 mM NaCl and having a pH of 6.5 – a more aggressive water used especially to test pipe samples for metal leaching and also for leaching of organic compounds at a lower pH value.

A.1.10.3 Materials

A.1.10.3.1 Pipe Samples

Pipe samples obtained from participating utilities and subsequently lined, except for the unlined control samples. The linings will be installed / applied by representatives of the manufacturers when possible, following their own procedures, so that the lining will conform to the manufacturer's specifications. For PET liners, this includes scraping, or pigging, the inner pipe walls to remove surface materials, if necessary, followed by the installation of the lining.

The pipes will then be promptly shipped back to the University of Kansas. (Overnight delivery is not necessary for PET-lined pipe specimens, since there is no “curing” involved as for coatings.) Upon receipt of the pipe samples at KU, they will be examined for damage to the pipe or the end-fittings. Pipes with significant damage may be removed from the experiment at this time. The fill-and-dump experiments will begin promptly once the coated or lined pipe samples are received. If enough samples are available, however, some of the pipe samples may be set aside for later experiments. For all tests, control samples consisting of an unlined lead pipe and an unlined copper pipe will also be used. The control samples will remain at KU throughout the coating or lining process, to reduce shipping costs and to better maintain the control section in its native state, i.e., so that the results for the lined pipe sections can be compared to those from a relatively undisturbed pipe section and not to one that has been sand-blasted, scraped, or otherwise prepared for lining or coating.

A.1.10.3.2 Extraction Waters

Batches of extraction water (dechlorinated tap water, chlorinated pH 8 extraction water, and low-pH extraction water) will be prepared in advance of the fill-and-dump tests following the procedures outlined in the SOP for Preparing Extraction Water for Fill-and-Dump Tests (Ver. 2.0). These waters will be allowed to reach room temperature prior to use in the fill-and-dump experiments. Samples of the dechlorinated tap water will be collected and analyzed for pH, dissolved oxygen, conductivity, alkalinity, and total chlorine prior to use. Additional samples of dechlorinated tap water will be collected and stored for analysis of total hardness, major anions, TOC, lead, copper, antimony and any other relevant metals, as these analyses may be conducted after the fill-and-dump experiments have been carried out. Samples of the chlorinated pH 8 extraction water and the low-pH extraction water will be collected for analysis of all analytes to be determined on extracts. All sample collection, storage, and analysis procedures will be conducted following the relevant SOPs.

A.1.10.4 Experimental Procedure

A.1.10.4.1 Preparation

After the pipe samples are inspected (as described above), the pipe nipples on each end should be thoroughly rinsed with tap water and wiped with a clean laboratory towel (WypAll X60) to remove any loose residues potentially containing lead, copper, antimony, or other substances, including organic contaminants.

Pipe samples will be flushed with cold tap water for 15 minutes to remove any particles or other debris from the interior of the pipe surfaces. The exact flushing time actually used will be recorded, and should be consistent among individual pipe samples within each fill-and-dump experiment. The pipe samples may be flushed individually or connected in series, but the control pipe samples (having potentially high lead or copper levels) should occupy the last position when placed in series. When connecting pipe samples to the flushing manifold, handle them carefully to avoid damaging the lining or coating. Be especially careful not to twist the pipe nipples, which could create a gap in the lining or coating and expose Pb or Cu metal to the extraction water. Hand tighten all connections if possible. If a wrench is needed to stop a leak, use two wrenches – one to hold the pipe nipples stationary and the other to tighten the fitting.

The flushing water will be discharged directly into the sink, and will not be retained for analysis. Following flushing, each pipe sample will be rinsed with at least 100 mL of the desired extraction water and then filled with that same water. The pipe samples will then be sealed with HDPE stoppers, using PTFE tape when necessary to prevent leaks, and the date and time will be recorded as the start time for the fill-and-dump experiment for that pipe section.

A.1.10.4.2 Design of the Test Matrix

Fill-and-dump tests will be conducted for different lengths of time on different pipe sections to determine the impact of contact time on leaching of metal and organic compounds. The specific schedule for each set of tests will be determined prior to beginning the fill-and-dump experiment and will depend on the total number of pipe samples available. In each case, similar experiments will be carried out using dechlorinated tap water and chlorinated extraction water. At least one test condition will be carried out in duplicate to examine the reproducibility

of our results. For the second set of experiments, we anticipate having at least seven lined pipe sections available for both the lead and copper pipes, along with one control pipe of each material. The full test matrix for this experiment is shown below (Table A.1.10.1). This matrix will be applied to both the lead and copper pipe sections, with the fill-and-dump experiments for each type of pipe being conducted simultaneously.

Table A.1.10.1 Holding times and fill solutions for FD-03

	Dechlorinated Tap Water		**Chlorinated Water**
Holding Time	**# of Lined Sections**	**# of Control Sections**	**# of Lined Sections**
6 hours	2	1	1
24 hours	1	--	1
4 days	1	--	1

A.1.10.4.3 Collection of Water for Analysis

At the end of the designated reaction time for each pipe section, one end of the pipe section will be unsealed. The water within that pipe section will then be poured into a glass beaker that has been pre-cleaned and drip-dried. The pre-cleaning method will consist of 1) rinsing with ethanol to remove any organic compounds; 2) rinsing with RO water; 3) immersion in an HCl acid bath for 2–24 hours; 4) rinsing with RO water; and 5) rinsing with reagent water. Beakers that are reused from one test to another will be cleaned in the same manner. Due to the anticipated high levels of lead or copper (and possible lead or copper particles) in the control pipe sections, special beakers will be designated for use with the control pipe sections only. These beakers will be cleaned between uses using Liquinox detergent and water to remove particles, then rinsed in the same manner as the other beakers.

A.1.10.4.3.1 Sections with dechlorinated tap water

Once in the beaker, sub-samples of this water will then be poured out and collected for analysis as follows:

Table A.1.10.2 Sample volumes for analysis in FD-03

Method	Volume	Storage	Notes
pH	20 mL	50 mL beaker	Analyze immediately
Lead and Copper	10 mL	PE test tube	Preserve with nitric acid
Metals by ICP	20 mL	PE test tube	Preserve with nitric acid
Total Organic Carbon	40 mL*	EPA vial	Preserve with H_3PO_4 to pH ~ 2

*If limited volume available, collect only 30 mL

The remaining sample will be transferred to a 4-oz. (120 mL) glass bottle with a PTFE-lined cap for analysis of organic compounds. An additional 10 mL sample will be collected from the control pipe and stored for lead and copper analysis in case a filtered sample is needed for dissolved metals. Excess sample beyond that needed for organic analysis will be used to obtain backup samples for other tests as needed.

A.1.10.4.3.2 Sections with chlorinated pH 8 extraction water

Once in the beaker, sub-samples of this water will then be poured out and collected for analysis as follows:

Table A.1.10.3 Storage conditions for samples after FD-03 holding times.

Method	Volume	Storage	Notes
pH	20 mL	50 mL beaker	Analyze immediately
Lead and Copper	10 mL	PE test tube	Preserve with nitric acid
Metals by ICP	20 mL	PE test tube	Preserve with nitric acid
TOC	40 mL*	EPA vial	Preserve with H_3PO_4 to pH ~2
Free chlorine	50 mL	150-mL beaker	Analyze immediately
Organic Compounds	≥102 mL	4-oz. glass vial w/ PTFE lined cap	Dechlorinate immediately; analyze ASAP

*If limited volume available, collect only 20-30 mL

† Dechlorinate by adding 1-2 drops of one of the dechlorinating solutions described in the SOP for preparing extraction waters, and preserve by adding 3 drops of concentrated HNO_3 per 50–60 mL sample.

Any remaining sample will be transferred to a glass bottle, for analysis of organic compounds, and will be immediately dechlorinated by adding, to each 100 mL of sample, 2 drops of a 1/10th dilution of one of the dechlorinating solutions described in the SOP for preparing extraction waters. Check immediately to verify that the residual chlorine has been quenched; if not, add additional 1/10th-strength dechlorinating solution dropwise until the sample is dechlorinated. Excess sample beyond that needed for organics analysis will be used as backup samples for other tests as needed.

A.1.10.4.4 Metal Leaching Tests

Leaching tests with the low-pH (6.5) extraction water will be conducted on two pipe sections of each type following the initial fill-and-dump tests. For both lead and copper pipes, one of the pipe samples filled with dechlorinated tap water for 6 hours and one filled with chlorinated pH 8 extraction water will be used for these tests, as well as the control (uncoated) pipe section. This test will begin the day after the six hour fill-and-dump tests are completed. The pipe sections will be flushed with 100 mL of pH 6.5 water to remove any water from the initial fill-and-dump tests. Then each pipe section will be filled with pH 6.5 water and sealed. After six hours, the water will be poured from the pipe into a glass beaker. Sub-samples of the water will be collected for analysis as described above for sections containing dechlorinated tap water.

Following the 6-hour fill-and-dump test with pH 6.5 water, the same pipe sections will be flushed again with 100 mL of pH 6.5 water. They will then be filled with pH 6.5 water, resealed, and left for one week. At the end of that time, the sections will be emptied and subsamples collected for analysis in the same manner described above for sections containing dechlorinated tap water.

A.1.10.4.5 Long-Term Organic Leaching Tests

Upon completion of the 24 hour fill-and-dump tests, the same pipe sections will be rinsed with 100 mL of either dechlorinated tap water or chlorinated extraction water (whichever they previously contained), refilled with the same water and sealed. These sections will be left for 4 days. At the end of that time, the sections will be emptied and subsamples collected for analysis in the appropriate manner for the specific water as described above.

A.1.10.4.6 Storage of Pipe Sections After Use

Pipe sections not being reused within 24 hours will be drained and allowed to dry before being resealed with vinyl end caps. Pipe sections being reused within 24 hours for additional testing (including the metal leaching tests and long-term organic leaching tests described below) will be drained and stored while still damp by sealing the ends with vinyl end caps.

A.1.10.4.7 Room Temperature

Record the room temperature in your lab notebook at least twice each day (a.m. and p.m.) when tests are in progress. If the room temperature drop below 20 °C or rises above 25 °C, attempt to remedy the problem (e.g., by adjusting the thermostat or opening a door or window) and notify the PI or a co-PI.

A.1.10.5 Reporting and Labeling

Each lined pipe section, as well as all control sections used in the fill-and-dump experiments, will be assigned a unique identifier. This identifier will consist of the letter Pb or Cu (for lead and copper pipes, respectively) and a number. For FD-03, this number will increment from Pb11 and Cu11 and no number will be reused. For each section the date of initial coating will be recorded, as well as the dates and nature (type of water, length of time) for any fill-and-dump experiment that pipe participated in. These data will be recorded in a spreadsheet to allow for tracking of the full experimental history of each pipe section. Any additional observations on the pipe section (damage, corrosion, etc.) will be noted in the same spreadsheet.

Each fill-and-dump experiment will be assigned an experiment number that will be recorded in the laboratory notebook. Experiment numbers for fill-and-dump experiments will be of the format FD-YY-Date, where FD refers to a fill-and-dump experiment, YY is the incremental number of the experiment and Date is the start date of the experiment. All aqueous samples collected during the fill-and-dump experiments will be labeled with the experiment number followed by the sample identification (ID) number. Sample ID numbers will be recorded in the laboratory notebook along with a full description of the sample. These

sample ID numbers will also be used in any electronic files produced during analysis of the sample.

A.1.10.6 Retesting of Samples Due to Compromised End-Fittings

Based on leaks observed during flushing of the PET-lined pipe specimens, a review of the preliminary results, and discussions with the vendor, it was determined that some of the test results, especially those for lead and copper, had been compromised. The end-fittings used, which were provided by the research team and were not consistent with the vendor's standard practices, allowed flushing and/or extraction water to pass behind the liner and to directly contact the pipe wall and to become contaminated with Pb, Cu, and perhaps other metals. During the time the ends of the pipe specimens were stoppered, the stoppers inserted into the end-fittings most likely prevented contaminated water from coming into direct contact with the extraction water. However, contaminated water could have seeped up around the rims of the end-fittings, not only before the pipe specimens were stoppered but also after the stoppers were removed and as the extraction water was being dumped out, thereby contaminating the samples. To address this problem, the end-fittings were removed from 10 pipe specimens (5 LSLs and 5 CSLs), two of which were the same controls used earlier and two of which were lined specimens that had not been used in previous tests. All these specimens were re-extracted only with low-pH reagent water.

The previously used pipe specimens were stored wet (and were not dried as specified in the above protocol), and the previously unused specimens were still dry, as they had not been used since being received from the vendor. The end-fittings were removed from the previously used specimens, exposing several inches of the PET liner on both ends of each pipe. Since it was possible that the pipe liner itself had become contaminated with Pb, Cu, or other materials from the pipe surfaces, the ends of each liner were cleaned by applying a Wypall L30 wipe dampened with 0.5% HCl to the outside. A separate wipe, dampened with reagent water, was applied to provide a second wipe and to remove any HCl. The wiping motion was designed to focus on the rim first, moving to the outer liner surface. Separate wipes were used to clean the inner wall of the liner with 0.5% HCl followed by reagent water, focusing on the inner wall before wiping the outer rim. The previously used pipe specimens were not flushed again, as

there was no obvious way to accomplish this in the absence of the end-fittings without risking additional sources of contamination. Instead, each pipe specimen was rinsed with 150 mL of pH 6.5 reagent water, first from one end of the pipe and then the other (300 mL total). Then, as each pipe was filled, it was first flushed with 200 mL of pH 6.5 reagent water using a fill-and-dump technique.

The previously unused pipe specimens were flushed for 15 min. with tap water (standard protocol) and the end-fittings were then immediately removed and the exposed ends of the PET liner were then cleaned as for the other specimens.

For this retesting, only pH 6.5 reagent water was used, with an initial exposure time of 6 h followed by refilling and an exposure time of 4 d. New stoppers, freshly cleaned, were used to avoid any contamination potentially associated with the previously used stoppers, which were in direct contact with the rims of the end-fittings and may have been heavily contaminated.

A.1.11 FD1 Matrix Spikes

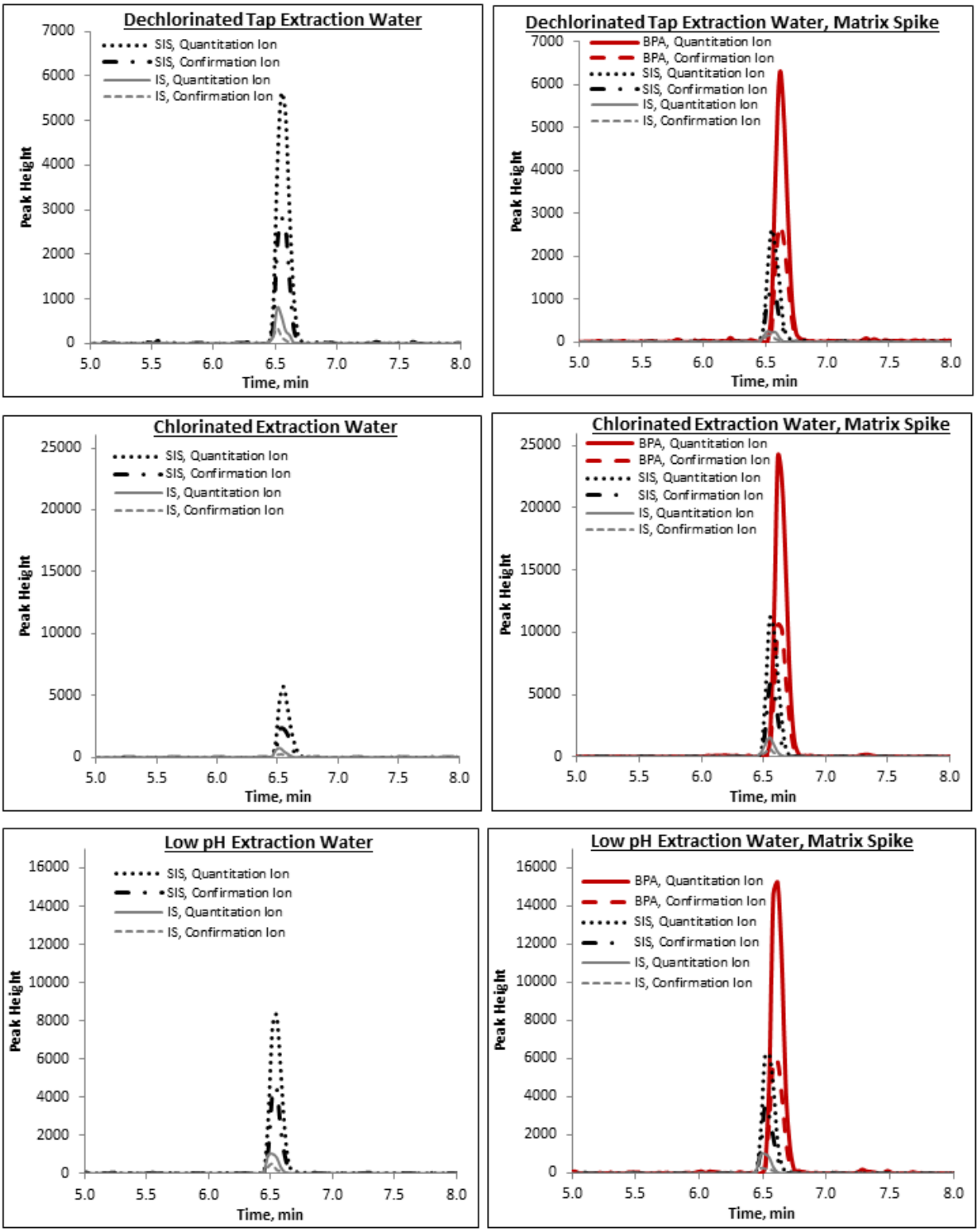


Figure A.1.11.1 Extraction waters for filling pipe sections from FD1 before and after the addition of a 40 µg/L BPA standard matrix spike.

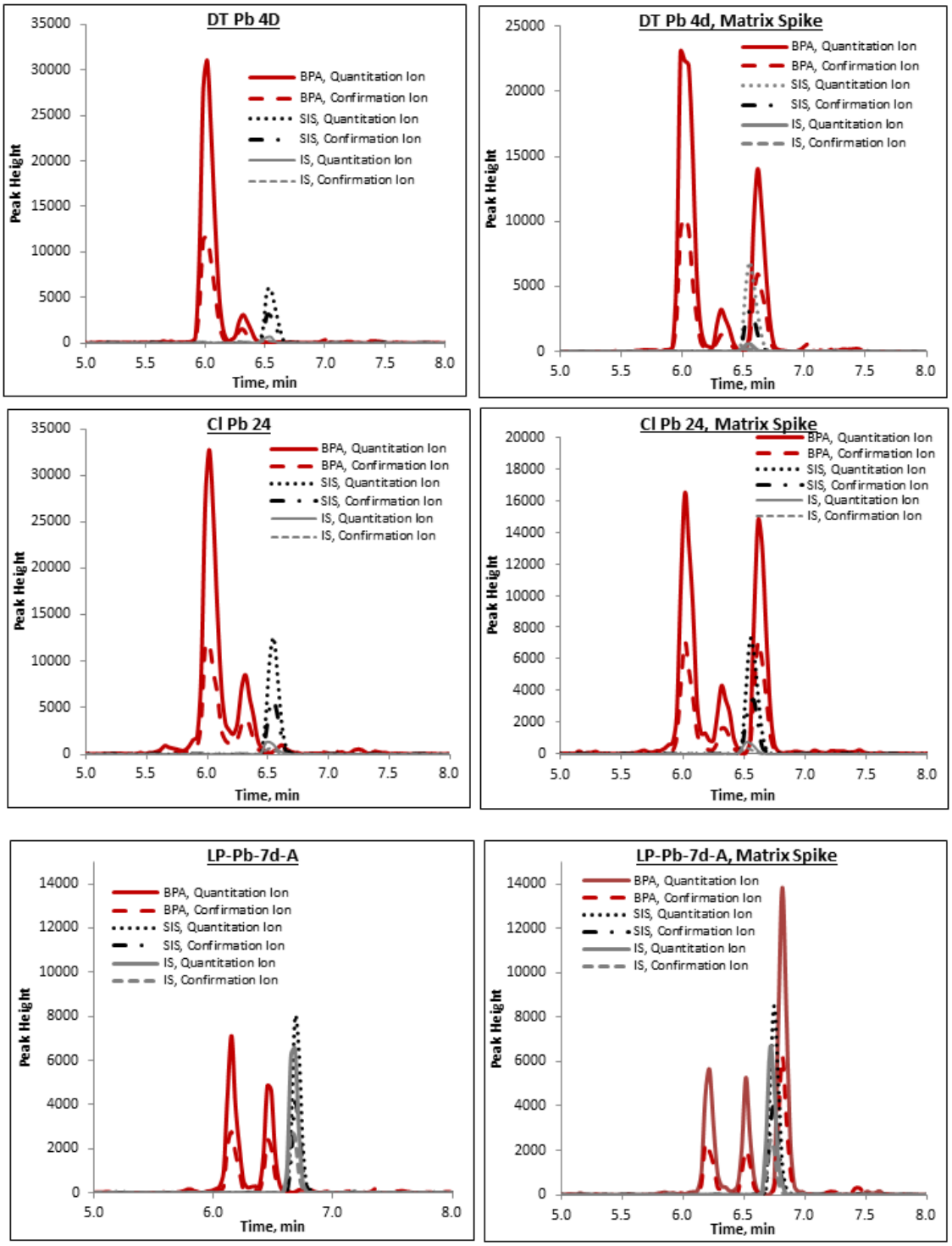


Figure A.1.11.2 Samples from FD1 with a BPA-like compound present before and after the addition of a 40 µg/L BPA standard matrix spike. DT-Pb-4D is an epoxy-coated LSL section filled with dechlorinated pH 8 tap water and held for 4 days. Cl-Pb-24 is an epoxy-coated CSL section filled with chlorinated pH 8 extraction water and held for 24 hours. LP-Cu-7D is an epoxy-coated CSL section filled with low pH extraction water and held for 7 day

A.1.12 FD2 Matrix Spikes

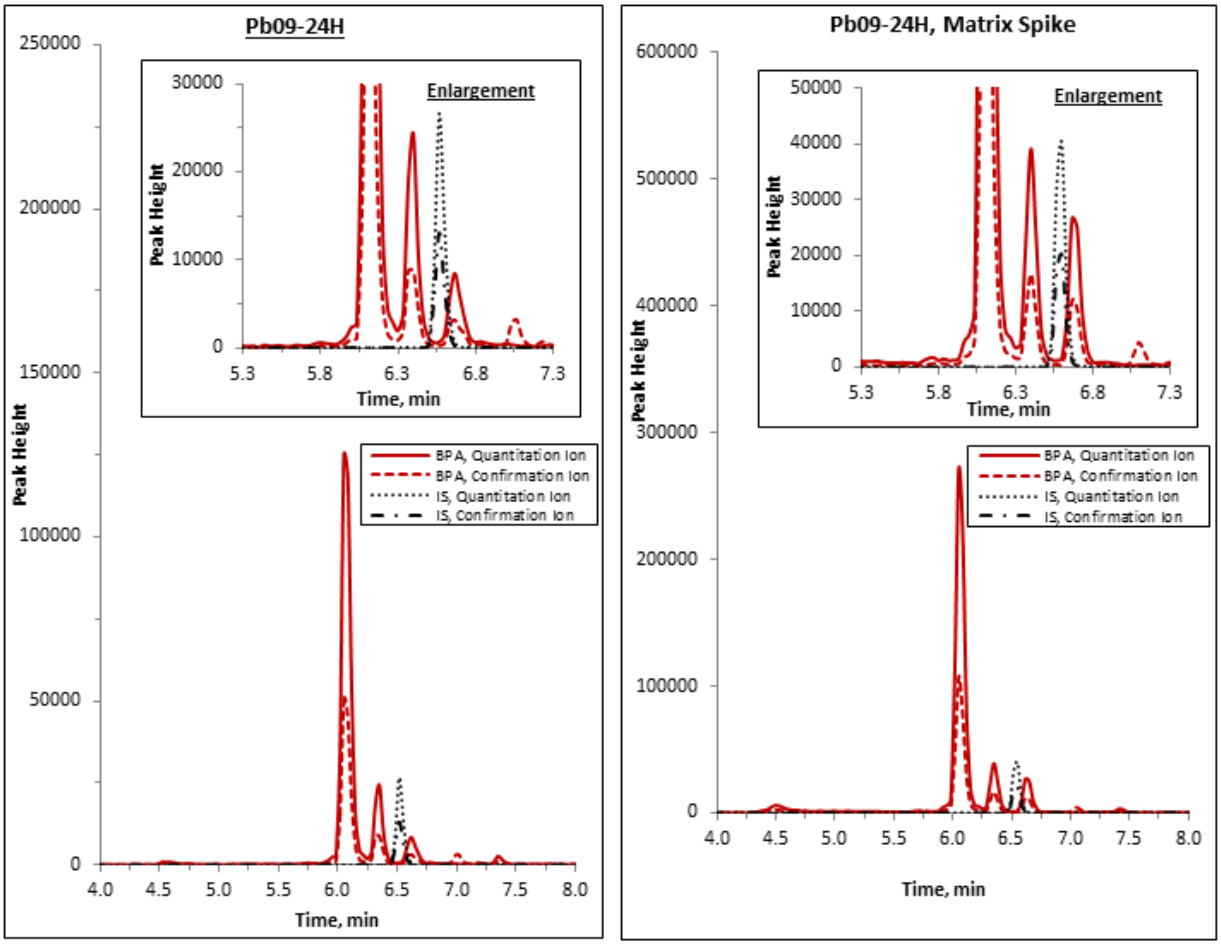


Figure A.1.12.1 Sample from FD2 with a BPA-like compound present before and after the addition of a 20 µg/L BPA standard matrix spike. Pb09-24H is an epoxy-coated LSL section not used in FD1, unrinsed, filled with chlorinated pH 8 extraction water, and held for 24 hours.

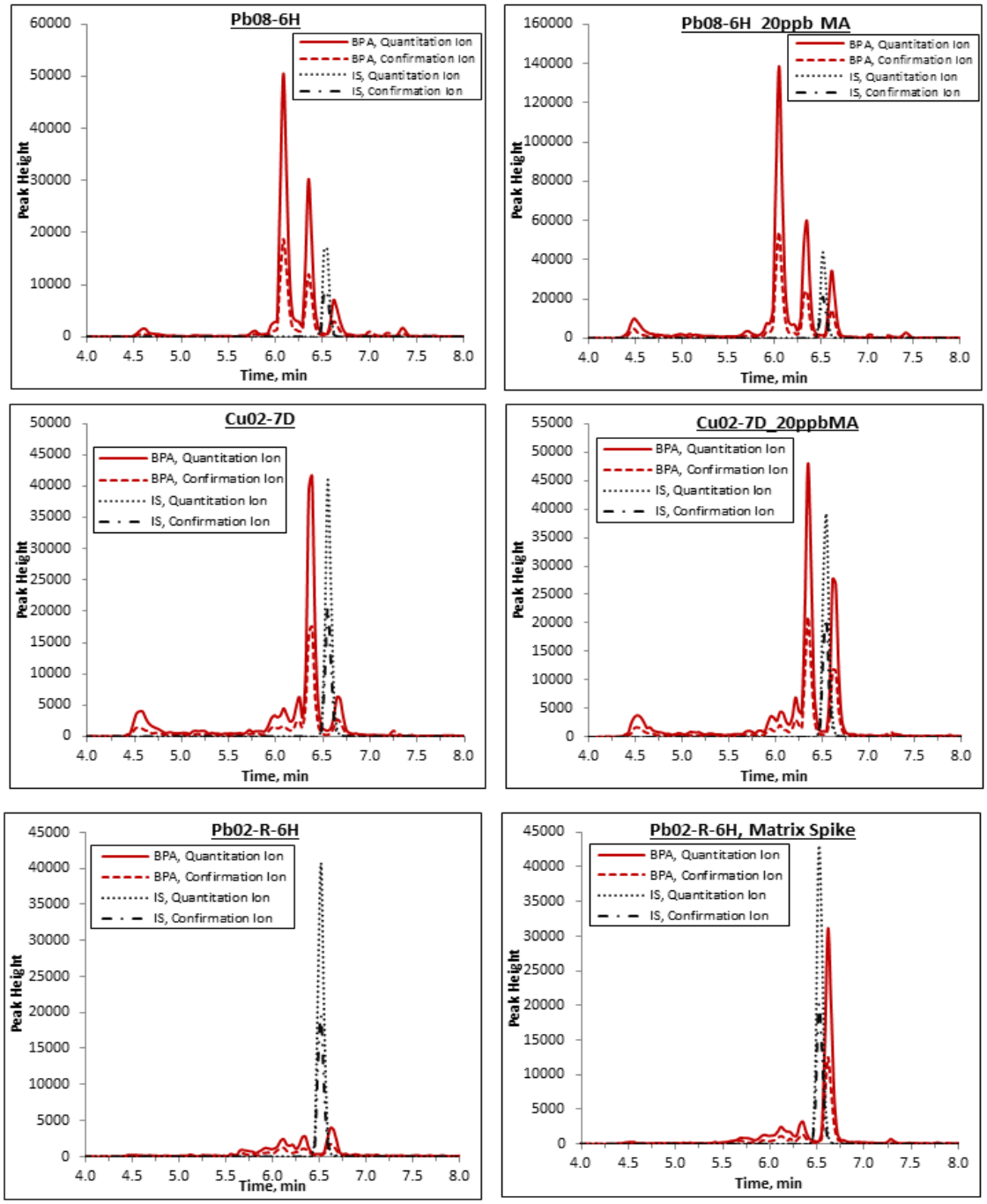


Figure A.1.12.2 Samples from FD2 before and after the addition of a 20 µg/L BPA matrix spike. Pb08-6H is an epoxy-coated LSL section filled with chlorinated pH 8 extraction water during FD1, stored dry for 7 mos., rinsed but unflushed, filled with chlorinated pH 8 extraction water, and held for 6 hours. Cu02-7D is an epoxy-coated CSL section, filled with dechlorinated pH 8 tap water and pH 6.5 extraction water during FD1, stored wet for 7 mos., rinsed but unflushed, filled with chlorinated pH 8 extraction water first for 24 h and then for 7 days). Pb02-R-6H is an epoxy-coated LSL section, filled with dechlorinated pH 8 tap water and pH 6.5 extraction water during FD1, stored wet for 7 mos., filled with chlorinated pH 8 extraction water for 24 h then 7d, flushed, and filled with chlorinated pH 8 extraction water and held for 6 hours.

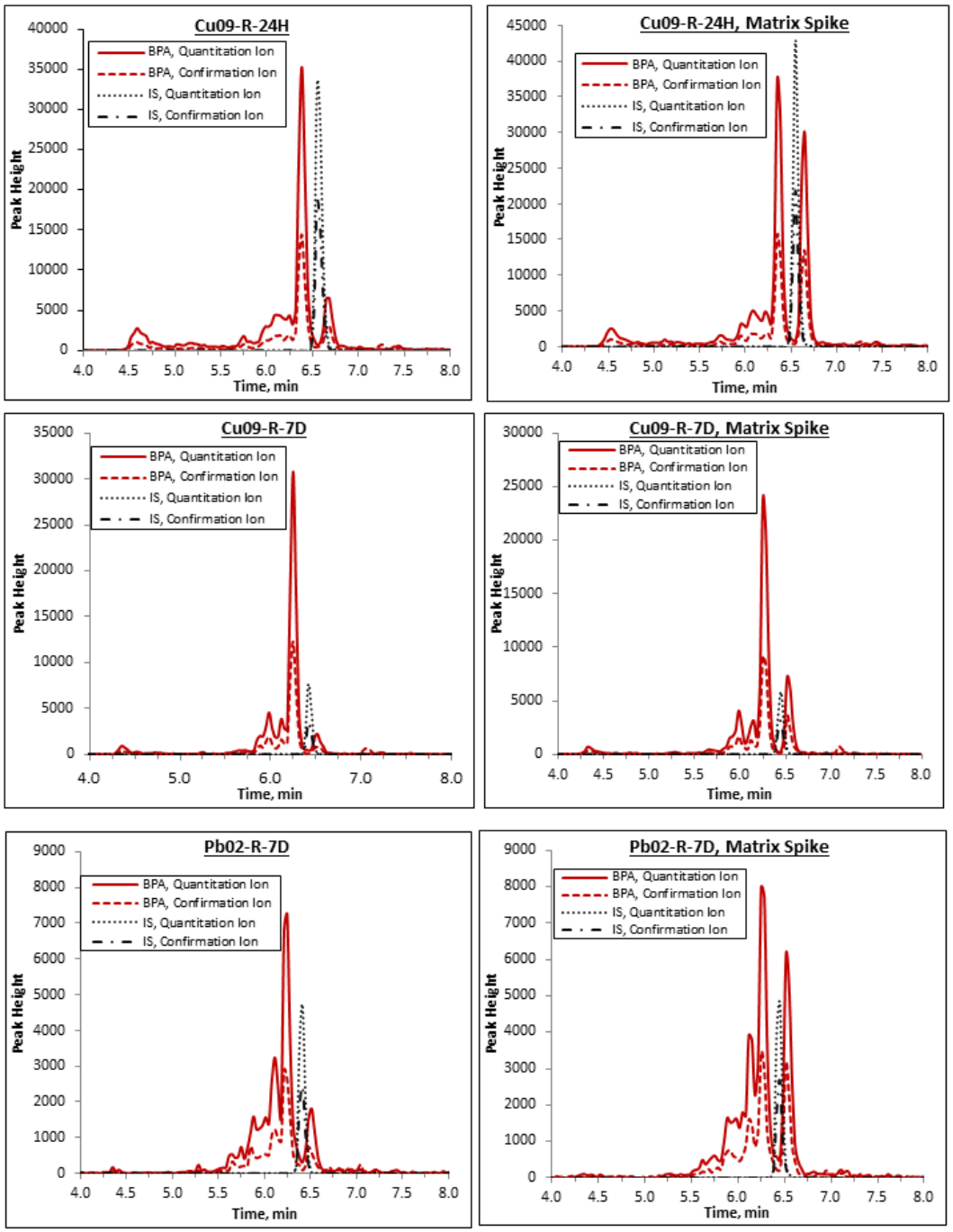


Figure A.1.12.3 Additional samples from FD2 before and after the addition of a 20 µg/L BPA matrix spike. Cu09-R-24H epoxy-coated CSL section unextracted in FD1, filled with chlorinated pH 8 extraction water for 24 h then 7d, flushed and filled with chlorinated pH 8 extraction water and held for 24 hours. Cu09-R-7D epoxy-coated CSL section unextracted in FD1, filled with chlorinated pH 8 extraction water for 24 h then 7d, flushed and filled with chlorinated pH 8 extraction water and held for 7 days. Pb02-R-7D epoxy-coated LSL section filled with dechlorinated pH 8 tap water and pH 6.5 extraction water during FD1, stored wet for 7 mos., flushed and filled with chlorinated pH 8 extraction water and held for 7 days.

A.2 Supplemental Information for Chapter 3: Epoxy Leachates with Similarity to Bisphenol A and Implications for Analysis

A.2.1 Supplemental Tables to Accompany Chapter 3

Table A.2.1.1 Experimental setup, sampling intervals, and results for the investigation of possible BPA adduct formation in contact with epoxy ingredient TETA, lead and copper ions, and salts of substances commonly present in drinking water.

Test Solution	pH	Sampling Interval	BPA-Like Compound Formation
20 mM TETA + 0.00035 mM BPA*	11.60	0, 1.3, 11.3, 18.0, 31.9, and 201 days	Detected at 11.3 and 18 days
20 mM TETA + 0.00035 mM BPA	7.42	0, 1.3, 11.3, 18.0, 31.9, and 201 days	Detected at 11.3 and 18 days
20 mM TETA + 0.00035 mM BPA	2.26	0, 1.3, 11.3, 18.0, 31.9, and 201 days	Detected at 11.3 and 18 days
62.5 mM FAS** + 0.00035 mM BPA	2.06	0, 1.3, 11.3, 18.0, 31.9, and 201 days	Not Detected
30 mM NH_4HCO_3 + 0.00035 mM BPA	3.75	0, 1.3, 11.3, 18.0, 31.9, and 201 days	Not Detected
498 mM $CaCl_2$ + 0.00035 mM BPA	7.10	0 and 13.2 days	Not Detected
407 mM $CuSO_4$ + 0.00035 mM BPA	4.00	0 and 13.2 days	Not Detected
80 mM $PbCl_2$ + 0.00035 mM BPA	2.34	0 and 13.2 days	Not Detected
547 mM $MgCl_2$ + 0.00035 mM BPA	5.08	0 and 13.2 days	Not Detected

* 80 µg/L BPA = 0.00035 mM BPA **FAS = ferrous ammonium sulfate

Table A.2.1.2 Additional data for the Fill-and-Dump Experiment 1 (FD1) investigating leaching from epoxy-coated pipe sections.

Extraction Water, Pipe Specimen, and Holding Time	BPA-Like Compound A, µg/L		BPA-Like Compound B, µg/L		BPA, µg/L		BADGE, µg/L	
	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs
Dechlorinated pH 8 Tap Water	ND	ND	ND	ND	≤ 0.057	≤ 0.057	≤ 7.0	≤ 7.0
Control (unlined) – 6 h	0.94	ND	ND	ND	0.37	0.33	≤ 7.0	≤ 7.0
Pipe01: 6 h (A)	36	52	ND	ND	≤ 0.057	≤ 0.057	340	32
Pipe02: 6 h (B)	49	62	ND	ND	≤ 0.057	≤ 0.057	214	36
Pipe05: 24 h	34	46	ND	ND	≤ 0.057	≤ 0.057	241	≤ 7.0
Pipe07: 4 d	68	54	5.6	6.3	≤ 0.057	≤ 0.057	≤ 7.0	≤ 7.0
Pipe05: 24 h, then 10 d	10	14	3.3	11	≤ 0.057	≤ 0.057	≤ 7.0	≤ 7.0
Chlorinated pH 8 Extraction Water	ND	ND	ND	ND	≤ 0.057	≤ 0.057	≤ 7.0	≤ 7.0
Pipe03: 6 h	37	7.4	9.4	ND	≤ 0.057	≤ 0.057	236	76
Pipe06: 24 h	51	59	12	13	≤ 0.057	≤ 0.057	101	≤ 7.0
Pipe08: 4 d	94	20	20	11	≤ 0.057	1.3	≤ 7.0	≤ 7.0
Pipe06: 24 h, then 10 d	ND	11	51	23	≤ 0.057	2.0	≤ 7.0	≤ 7.0
pH 6.5 Extraction Water	ND	ND	ND	ND	≤ 0.057	≤ 0.057	≤ 7.0	≤ 7.0
Control (uncoated) initially filled with dechlorinated pH 8 tap water, held for 6 h, then refilled with pH 6.5 extraction water and held for:								
6 h	ND	ND	ND	ND	≤ 0.057	≤ 0.057	≤ 7.0	≤ 7.0
6 h, then refilled and held 7 d	ND	ND	ND	ND	≤ 0.057	≤ 0.057	≤ 7.0	≤ 7.0
Pipes initially filled with dechlorinated pH 8 tap water, held 6 h, then refilled with pH 6.5 extraction water and held for:								
Pipe01: 6 h (A)	11	14	ND	ND	≤ 0.057	≤ 0.057	≤ 7.0	≤ 7.0
Pipe02: 6 h (B)	7.4	11	2.5	1.7	0.82	≤ 0.057	≤ 7.0	≤ 7.0
Pipe01: 6 h, then 7 d (A)	16	8.8	11	10	0.58	0.26	≤ 7.0	≤ 7.0
Pipe02: 6 h, then 7 d (B)	15	13	7.8	6.3	≤ 0.057	≤ 0.057	≤ 7.0	≤ 7.0
Pipes initially filled with chlorinated pH 8 extraction water, held 6 h, then refilled with pH 6.5 extraction water and held:								
Pipe03: 6 h	9.0	8.2	4.0	5.1	1.3	≤ 0.057	13.3	≤ 7.0
Pipe03: 6 h, then 7 d	ND	11	12	13	0.79	≤ 0.057	≤ 7.0	≤ 7.0

LSLs = Lead service lines CSLs = Copper service lines ND = Not detected.

Table A.2.1.3 Additional data for fill-and-dump experiment 2 (FD2) investigating leaching from stored epoxy-coated pipe sections.

Extraction Water, Pipe Specimen, and Holding Time	BPA-Like Compound A, µg/L		BPA-Like Compound B, µg/L		BPA, µg/L		BADGE, µg/L	
	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs
Before flushing for 15 min								
Chlorinated pH 8 Extraction Water	ND	ND	ND	ND	0.22	0.22	≤ 7.0	≤ 7.0
Pipe08: 6 h	81	25	39	18	10	8.8	≤ 7.0	≤ 7.0
Pipe02: 24 h	13	5.1	14	12	10	9.8	≤ 7.0	≤ 7.0
Pipe05: 24 h	17	19	14	27	9	1.1	≤ 7.0	≤ 7.0
Pipe09: 24 h	150	161	29	33	10	2.3	≤ 7.0	≤ 7.0
Chlorinated pH 8 Extraction Water	ND	ND	ND	ND	0.059	0.059	≤ 7.0	≤ 7.0
Pipe02: 24 h, then 7d	4.4	8.6	26	31	2.8	1.2	≤ 7.0	≤ 7.0
Pipe05: 24 h, then 7d	5.6	15	26	53	2.6	2.4	≤ 7.0	≤ 7.0
Pipe09: 24 h, then 7d	125	58	38	71	2.1	2.2	≤ 7.0	≤ 7.0
After flushing for 15 min								
Chlorinated pH 8 Extraction Water	ND	ND	ND	ND	≤ 0.057	≤ 0.057	≤ 7.0	≤ 7.0
Pipe02: 6 h	2.2	3.5	1.8	2.0	0.83	ND	≤ 7.0	≤ 7.0
Pipe05: 6 h	4.1	6.9	1.7	7.8	0.24	0.75	≤ 7.0	≤ 7.0
Pipe08: 6 h	48	18	35	13	1.3	0.87	≤ 7.0	≤ 7.0
Pipe09: 6 h	20	11	17	12	2.2	≤ 0.057	≤ 7.0	≤ 7.0
Chlorinated pH 8 Extraction Water	ND	ND	ND	ND	0.035	0.035	≤ 7.0	≤ 7.0
Pipe02: 6 h, then 24 h	8.3	6.1	5.8	7.1	0.42	≤ 0.057	≤ 7.0	≤ 7.0
Pipe05: 6 h, then 24 h	3.7	6.7	3.8	22	0.52	1.6	≤ 7.0	≤ 7.0
Pipe08: 6 h, then 24 h	27	9.2	52	28	1.8	2.1	≤ 7.0	≤ 7.0
Pipe09: 6 h, then 24 h	9.4	6.9	24	28	1.2	1.8	≤ 7.0	≤ 7.0
Chlorinated pH 8 Extraction Water	ND	ND	ND	ND	0.038	0.038	≤ 7.0	≤ 7.0
Pipe02: 6 h, then 24 h, then 7d	30	21	44	76	12	10	≤ 7.0	≤ 7.0
Pipe05: 6 h, then 24 h, then 7d	32	ND	37	91	12	9.1	≤ 7.0	≤ 7.0
Pipe08: 6 h, then 24 h, then 7d	ND	ND	136	97	10	11	≤ 7.0	≤ 7.0
Pipe09: 6 h, then 24 h, then 7d	ND	ND	83	106	8.5	10	≤ 7.0	≤ 7.0

ND = Not detected LSLs = Lead service lines CSLs = Copper service lines

Table A.2.1.4 Additional minor BPA-like peaks observed during the fill-and-dump experiment 2 (FD2) investigating leaching from stored epoxy-coated pipe sections.

Extraction Water, Pipe Specimen, and Holding Time	BPA-Like, µg/L 4.4 min RT		BPA-Like, µg/L 5.7 min RT		BPA-Like, µg/L 5.9 min RT		BPA-Like, µg/L 7.4 min RT	
	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs
Before flushing for 15 min								
Chlorinated pH 8 Extraction Water	ND	ND	ND	ND	ND	ND	ND	ND
Pipe08: 6 h	9.9*	0.42*	1.9	ND	ND	0.37	1.1*	0.22
Pipe02: 24 h	0.14	0.21*	ND	ND	0.69	0.44*	ND	ND
Pipe05: 24 h	0.17*	6.8	ND	1.1*	ND	ND	ND	0.10*
Pipe09: 24 h	0.56	12*	ND	0.59	0.19	ND	0.58	1.6
Chlorinated pH 8 Extraction Water	ND	ND	ND	ND	ND	ND	ND	ND
Pipe02: 24 h, then 7d	2.6	5.8	0.68	0.17*	ND	ND	ND	ND
Pipe05: 24 h, then 7d	2.9	10*	ND	0.29*	ND	ND	ND	0.11*
Pipe09: 24 h, then 7d	9.5	16.3	0.35	0.37	ND	ND	1.4*	0.84*
After flushing for 15 min								
Chlorinated pH 8 Extraction Water	ND	ND	ND	ND	ND	ND	ND	ND
Pipe02: 6 h	ND	ND	0.51	0.37	ND	ND	ND	ND
Pipe05: 6 h	ND	1.9*	0.33	1.5*	ND	ND	ND	ND
Pipe08: 6 h	11	3.5*	1.0*	1.8	ND	ND	0.42*	ND
Pipe09: 6 h	2.6*	2.7	3.3	2.4*	ND	ND	0.18*	0.11*
Chlorinated pH 8 Extraction Water	ND	ND	ND	ND	ND	ND	ND	ND
Pipe02: 6 h, then 24 h	ND	0.20*	0.53	0.24*	ND	ND	ND	ND
Pipe05: 6 h, then 24 h	0.13	2.4*	2.67	0.55	ND	ND	ND	ND
Pipe08: 6 h, then 24 h	10	3.9*	ND	1.0*	ND	ND	0.66*	0.11*
Pipe09: 6 h, then 24 h	2.9	3.7	0.66	0.58	ND	ND	ND	0.20
Chlorinated pH 8 Extraction Water	ND	ND	ND	ND	ND	ND	ND	ND
Pipe02: 6 h, then 24 h, then 7d	1.4	2.7	3.6	ND	13	12*	ND	ND
Pipe05: 6 h, then 24 h, then 7d	1.2*	4.7	ND	ND	12	17	ND	ND
Pipe08: 6 h, then 24 h, then 7d	2.4*	6.3*	ND	3.2	58	27	ND	ND
Pipe09: 6 h, then 24 h, then 7d	3.9	5.4	ND	2.3*	28	27	ND	ND

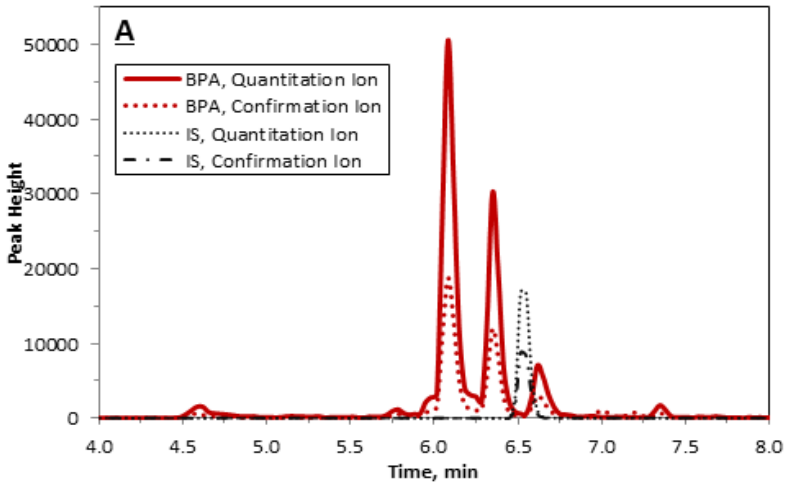
*Quantitation-to-confirmation ion ratio does not match BPA RT = Retention time ND = Not detected

Table A.2.1.5 BPA-like Compound A and BADGE-$2H_2O$ detected in extraction waters of the second epoxy-coating fill-and-dump experiment (FD2).

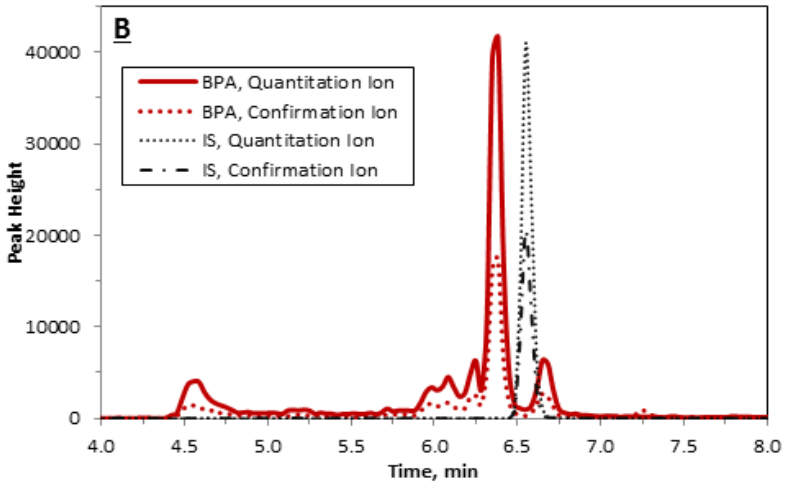
Extraction Water and Holding Time	BPA-like Compound A, µg/L		BADGE-$2H_2O$, µg/L	
	LSLs	CSLs	LSLs	CSLs
Chlorinated pH 8 Extraction Water (0 h)	ND	ND	≤ 1.0	≤ 1.0
Pipe08: 6 h	81	25	91	2.2
Pipe02: 24 h	13	5.1	1.8	0.83
Pipe05: 24 h	17	19	3.5	11
Pipe09: 24 h	150	161	231	≤ 1.0
Chlorinated pH 8 Extraction Water (0 h)	ND	ND	≤ 1.0	≤ 1.0
Pipe02: 24 h, then 7d	4.4	8.6	≤ 1.0	≤ 1.0
Pipe05: 24 h, then 7d	5.6	15	2.5	6.3
Pipe09: 24 h, then 7d	125	58	66	46
Reflushed, then:				
Chlorinated pH 8 Extraction Water (0 h)	ND	ND	≤ 1.0	≤ 1.0
Pipe02: 6 h	2.2	3.5	≤ 1.0	≤ 1.0
Pipe05: 6 h	4.1	6.9	≤ 1.0	≤ 1.0
Pipe08: 6 h	48	18	38	6.7
Pipe09: 6 h	20	11	≤ 1.0	2.8
Chlorinated pH 8 Extraction Water (0 h)	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0
Pipe02: 6 h, then 24 h	8.3	6.1	≤ 1.0	≤ 1.0
Pipe05: 6 h, then 24 h	3.7	6.7	≤ 1.0	≤ 1.0
Pipe08: 6 h, then 24 h	27	9.2	19	2.0
Pipe09: 6 h, then 24 h	9.4	6.9	1.9	≤ 1.0
Chlorinated pH 8 Extraction Water (0 h)	ND	ND	≤ 1.0	≤ 1.0
Pipe02: 6 h, then 24 h, then 7d	30	21	≤ 1.0	≤ 1.0
Pipe05: 6 h, then 24 h, then 7d	32	ND	1.1	1.5
Pipe08: 6 h, then 24 h, then 7d	ND	ND	21	5.4
Pipe09: 6 h, then 24 h, then 7d	ND	ND	6.5	5.8

* Assuming a response factor equivalent to BPA ND = Not detected

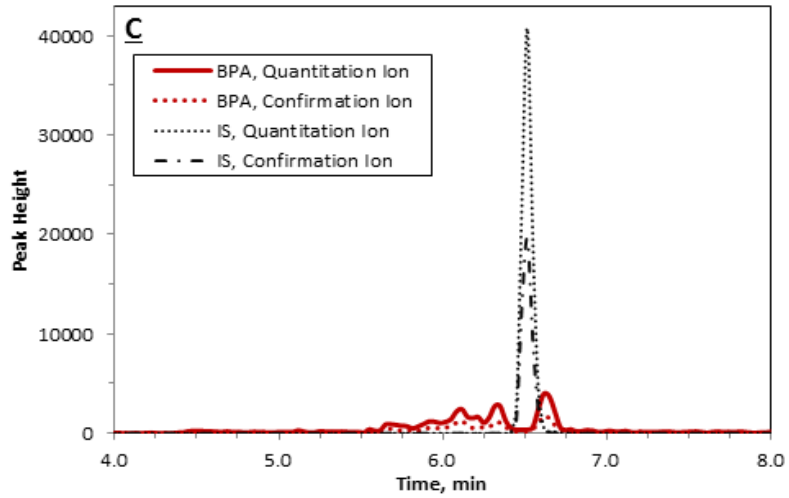
A.2.2 Supplemental Figures to Accompany Chapter 3



(A) Chromatogram from sample Pb08-6H (epoxy-coated LSL section filled with chlorinated pH 8 extraction water during FD1, stored dry for 7 mos., rinsed but unflushed, filled with chlorinated pH 8 extraction water, and held for 6 hours).



(B) Chromatogram from sample Cu02-7D (epoxy-coated CSL section, filled with dechlorinated pH 8 tap water and pH 6.5 extraction water during FD1, stored wet for 7 mos., rinsed but unflushed, filled with chlorinated pH 8 extraction water first for 24 h and then for 7 days).



(C) Chromatogram from sample Pb02-R-6H (epoxy-coated LSL section, filled with dechlorinated pH 8 tap water and pH 6.5 extraction water during FD1, stored wet for 7 mos., filled with chlorinated pH 8 extraction water for 24 h then 7d, flushed, and filled with chlorinated pH 8 extraction water and held for 6 hours).

Figure A.2.2.1 LC/MS/MS chromatograms from FD2 illustrating BPA-like compounds with retention times differing from that of BPA (BPA retention time is 6.6 min).

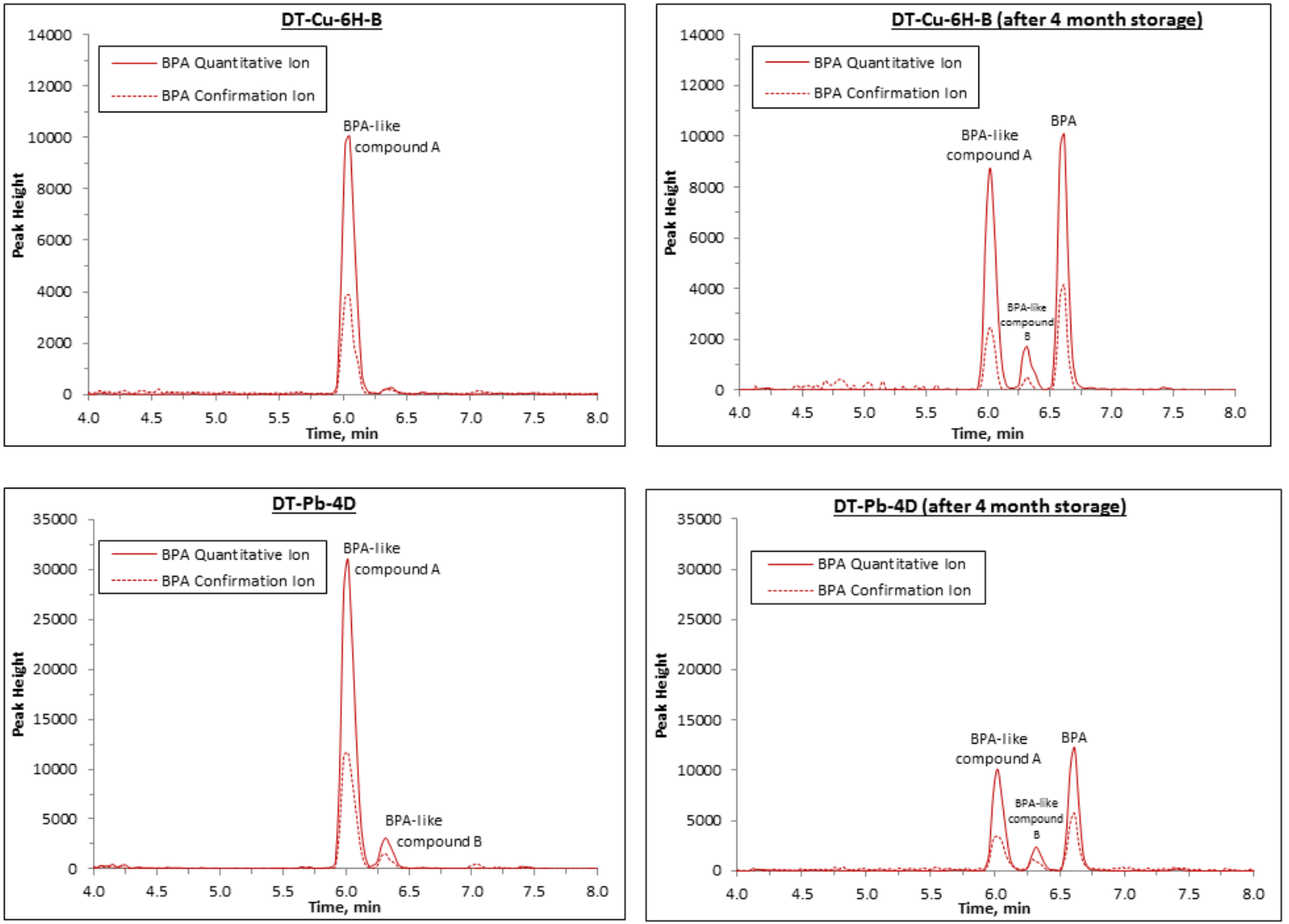


Figure A.2.2.2 LC/MS/MS chromatograms from FD1 illustrating a shift in BPA-like compound retention time after sample storage. DT-Cu-6H-B was an epoxy-coated CSL section filled with dechlorinated pH 8 tap water and held for 6 hours. DT-Pb-4D was an epoxy-coated LSL section filled with dechlorinated pH 8 tap water and held for 4 days.

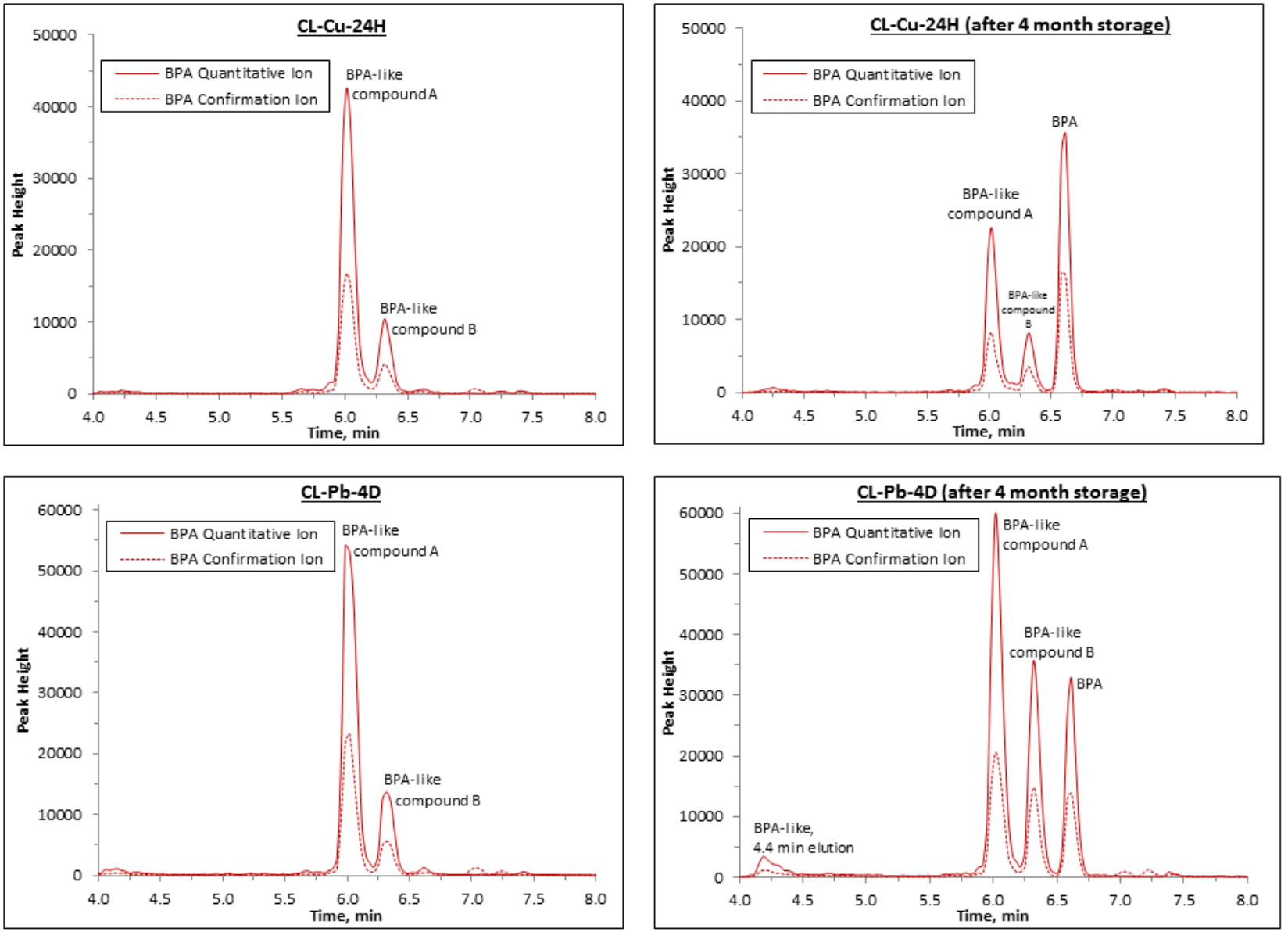


Figure A.2.2.3 LC/MS/MS chromatograms from FD1 illustrating a shift in BPA-like compound retention time after sample storage. CL-Cu-24H was an epoxy-coated CSL section filled with chlorinated pH 8 extraction water and held for 24 hours. CL-Pb-4D was an epoxy-coated LSL section filled with chlorinated pH 8 extraction water and held for 4 days.

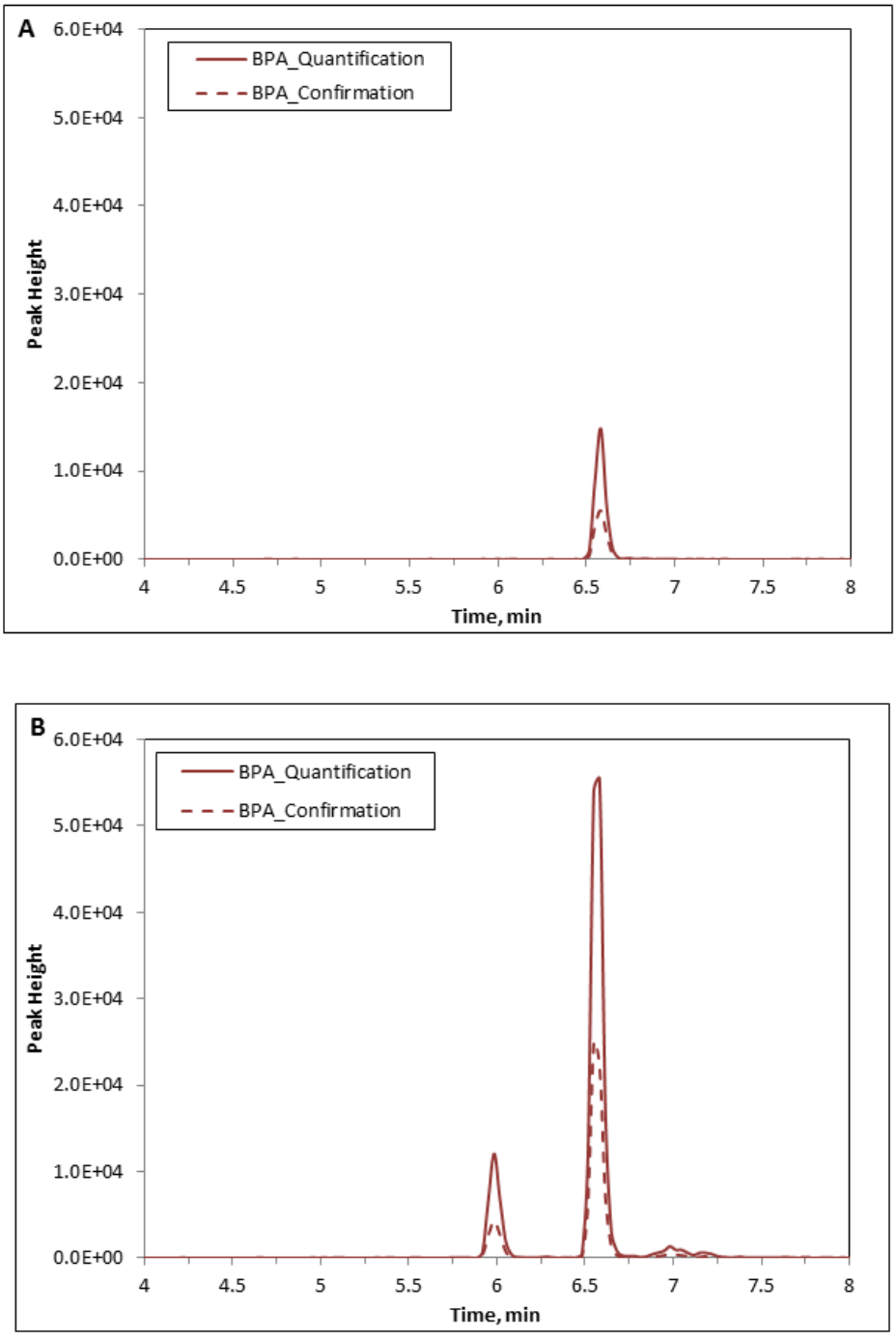


Figure A.2.2.4 Chromatogram of a 200 µg/L BADGE standard with free chlorine (1.5 mg/L as Cl_2) analyzed with the LC/MS/MS bisphenol method. (A) Sample after 1 min contact time. (B) Sample after 7 days of contact time.

A.3 Supplemental Information for Chapter 4: Bisphenol Diglycidyl Ethers and Bisphenol A and their Hydrolysis in Drinking Water

A.3.1 Supplemental Tables to Accompany Chapter 4

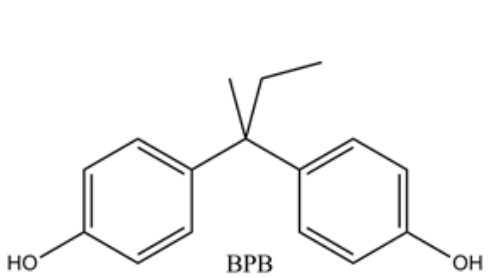
Table A.3.1.1 GC/MS Scan Method Parameters for Uncured Epoxy.

GC/MS Parameter	Setting
Injection	1.0 µm splitless
Injection Temperature	270°C
Carrier Gas	Helium
Transfer Line Temperature	270°C
Flow Rate	1.0 mL/min constant flow
Oven Temperature	100°C (hold for 0.5 min) Ramp at 9°C/min to 300°C
Solvent Delay	3.5 min
Solvent	Methanol
MS Scan	40 to 550 amu

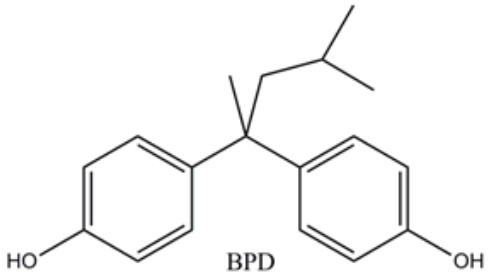
Table A.3.1.2 LC/MS/MS method parameters and Method Detection Limits (MDLs).

Compound	CAS Number	MS Ionization Mode	Precursor Ion m/z		Product Ion, m/z	Declustering Potential (V)	Collision Energy (V)	Collision Cell Exit Potential (V)	MDL µg/L
BPB	77-40-7	negative	**[M-H]⁻**	**241.0**	**212.0**	-66.980	-24.200	-9.440	0.18
			[M-H]⁻	241.0	211.0	-66.980	-34.760	-13.100	
BPD	6807-17-6	negative	**[M-H]⁻**	**269.0**	**212.0**	-82.070	-25.080	-16.670	0.10
			[M-H]⁻	269.0	211.0	-82.070	-35.560	-3.600	
BPE	2081-08-5	negative	**[M-H]⁻**	**213.0**	**198.0**	-68.210	-23.370	-3.020	0.070
			[M-H]⁻	213.0	199.0	-68.210	-37.540	-3.440	
BPF	620-92-8	negative	**[M-H]⁻**	**199.0**	**93.0**	-67.190	-29.070	-6.880	0.18
			[M-H]⁻	199.0	105.0	-70.680	-28.420	-5.560	

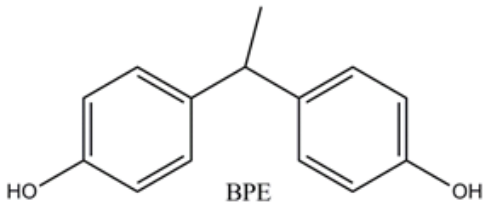
transitions in bold are quantitation ions



BPB



BPD



BPE

Table A.3.1.3 BADGE leached into extraction waters in fill-and-dump tests on epoxy-coated lead and copper pipe specimens.*

Extraction Water and Holding Time	BADGE, µg/L	
	Lead Pipe	**Copper Pipe**
Dechlorinated Tap Water, fill solution	≤ 7.0	≤ 7.0
Control (unlined) – 6 hours	≤ 7.0	≤ 7.0
6 hours	227.1	34.1
24 hours	241.1	≤ 7.0
4 days	≤ 7.0	≤ 7.0
24 hours, then 10 days	≤ 7.0	≤ 7.0
Chlorinated Reagent Water, fill solution	≤ 7.0	≤ 7.0
6 hours	235.5	76.4
24 hours	101.2	≤ 7.0
4 days	≤ 7.0	≤ 7.0
24 hours, then 10 days	≤ 7.0	≤ 7.0
Low pH Reagent Water, fill solution	≤ 7.0	≤ 7.0
Control (unlined) 6 Hours Dechlorinated Tap Water, then:		
6 hours	≤ 7.0	≤ 7.0
6 hours, then 7 days	≤ 7.0	≤ 7.0
6 Hours Dechlorinated Tap Water, then:		
6 hours	≤ 7.0	≤ 7.0
6 hours, then 7 days	≤ 7.0	≤ 7.0
6 Hours Chlorinated pH 8 Reagent Water, then:		
6 hours	≤ 7.0	≤ 7.0
6 hours, then 7 days	≤ 7.0	≤ 7.0

* See Breault et al., 2013 and Lane et al., 2013 for experimental details.

Table A.3.1.4 Experimentally determined rate constants (k'_{Hyd}) for BADGE at 25 and 40 °C.

pH	Temp (°C)	k'(Hyd, exp) (1/s)	Mean	%RSD
2.11	40	1.38E-04	1.33E-04	5.55
2.11	40	1.27E-04		
2.96	40	2.51E-05	2.51E-05	0.38
2.96	40	2.50E-05		
4.64	40	7.23E-06	7.23E-06	0.00
4.64	40	7.23E-06		
5.66	40	7.32E-06	7.33E-06	0.11
5.66	40	7.33E-06		
7.14	40	7.63E-06	6.62E-06	19.2
7.14	40	7.75E-06		
7.19	40	5.89E-06		
7.19	40	5.20E-06		
8.38	40	6.26E-06	6.37E-06	2.59
8.38	40	6.49E-06		
10.53	40	9.40E-06	9.17E-06	3.46
10.53	40	8.95E-06		
11.06	40	8.53E-06	8.54E-06	0.21
11.06	40	8.56E-06		
2.00	25	3.90E-05	4.19E-05	9.92
2.00	25	4.49E-05		
3.14	25	4.29E-06	4.39E-06	3.10
3.14	25	4.48E-06		
4.38	25	2.01E-06	1.97E-06	4.70
4.38	25	1.84E-06		
4.58	25	2.06E-06		
4.58	25	1.96E-06		
7.17	25	1.58E-06	1.88E-06	23.7
7.17	25	1.55E-06		
7.18	25	2.51E-06		
7.18	25	1.91E-06		
10.84	25	2.23E-06	2.10E-06	8.62
10.84	25	1.97E-06		
11.71	25	3.82E-06	3.93E-06	3.78
11.71	25	4.03E-06		

Table A.3.1.5 Experimentally determined rate constants (k'_{Hyd}) for BADGE at 15°C.

pH	k'(hyd, exp) (1/s)	Mean	%RSD
2.02	1.23E-05	1.23E-05	0.29
2.02	1.23E-05		
2.57	4.83E-06	4.77E-06	7.3
2.57	5.24E-06		
2.60	4.42E-06		
2.60	4.62E-06		
3.25	1.22E-06	1.19E-06	3.04
3.25	1.16E-06		
4.42	8.42E-07	8.78E-07	5.84
4.42	9.14E-07		
5.67	9.90E-07	1.17E-06	21.9
5.67	1.35E-06		
7.18	7.56E-07	6.87E-07	8.0
7.18	6.33E-07		
7.26	7.06E-07		
7.26	6.55E-07		
10.81	1.00E-06	9.78E-07	3.77
10.81	9.52E-07		
12.00	1.28E-06	1.40E-06	12.4
12.00	1.52E-06		

Table A.3.1.6 The experimentally determined rate constants for BFDGE isomers and the isomeric sum. Percent relative standard deviation and alpha values were determined to assess significance.

	k'(hyd, exp) (1/s)					
pH	***p,p'*-BFDGE**	***o,p'*-BFDGE**	***o,o'*-BFDGE**	**Mean k**	***RSD (%)***	***α***
2.21	3.24E-05	3.16E-05	3.58E-05	3.43E-05	8.37	0.08
2.21	3.43E-05	3.23E-05	3.92E-05			
3.96	2.42E-06	1.99E-06	1.68E-06	2.00E-06	30.7	0.07
3.96	3.00E-06	1.60E-06	1.33E-06			
7.17	1.67E-06	2.10E-06	1.20E-06	1.59E-06	26.6	0.008
7.17	1.60E-06	1.94E-06	1.00E-06			
9.08	1.48E-06	1.82E-06	1.43E-06	1.50E-06	14.7	0.07
9.08	1.33E-06	1.68E-06	1.23E-06			
11.56	2.15E-06	2.37E-06	1.89E-06	2.12E-06	10.7	0.003
11.56	2.20E-06	2.32E-06	1.81E-06			

A.3.2 Supplemental Figure to Accompany Chapter 4

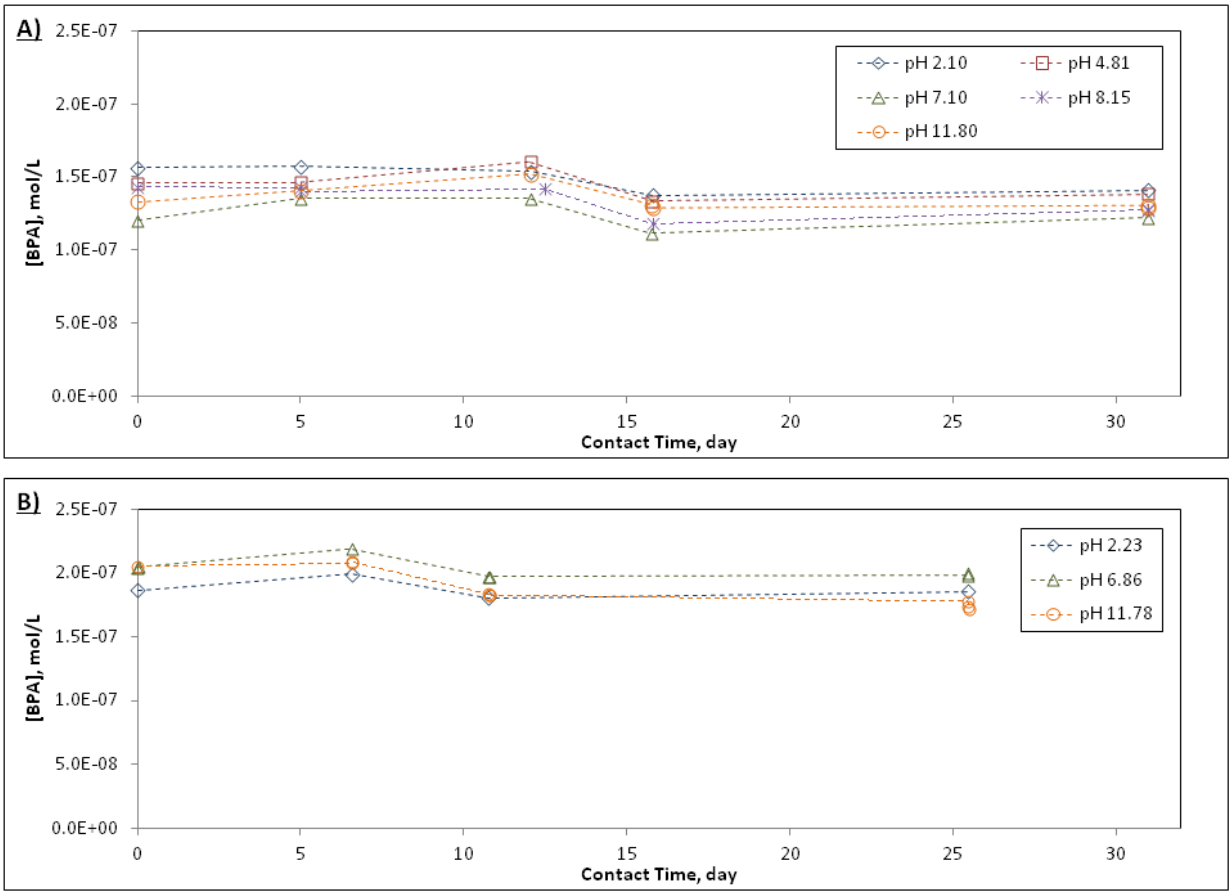


Figure A.3.2.1 Hydrolysis study of BPA in phosphate buffered water. Plot A tracks the minimal decay of BPA over time at 25 °C. Plot B tracks the minimal decay of BPA over time at 40 °C.

A.4. Supplemental Information for Chapter 5: Chlorination and Chloramination of Bisphenol A, Bisphenol F, and Bisphenol A Diglycidyl Ether in Drinking Water

A.4.1 Supplemental Table to Accompany Chapter 5

Table A.4.1.1 Approximate half-lives for oxidation of BPA and BPF with monochloramine at pH values of 7.6 and 9.1 and temperates of 25 °C and 10 °C. Monochloramine was applied at approximately 3.5 mg/L as Cl_2.

	Approximate Half-Lives			
	25 °C		10 °C	
	pH 7.6	pH 8.9	pH 7.6	pH 8.9
BPA	17 hours	1.8 days	2.6 days	8.8 days
BPF	19 hours	23 hours	2.0 days	1.5 days

A.4.2 Supplemental Figures to Accompany Chapter 5

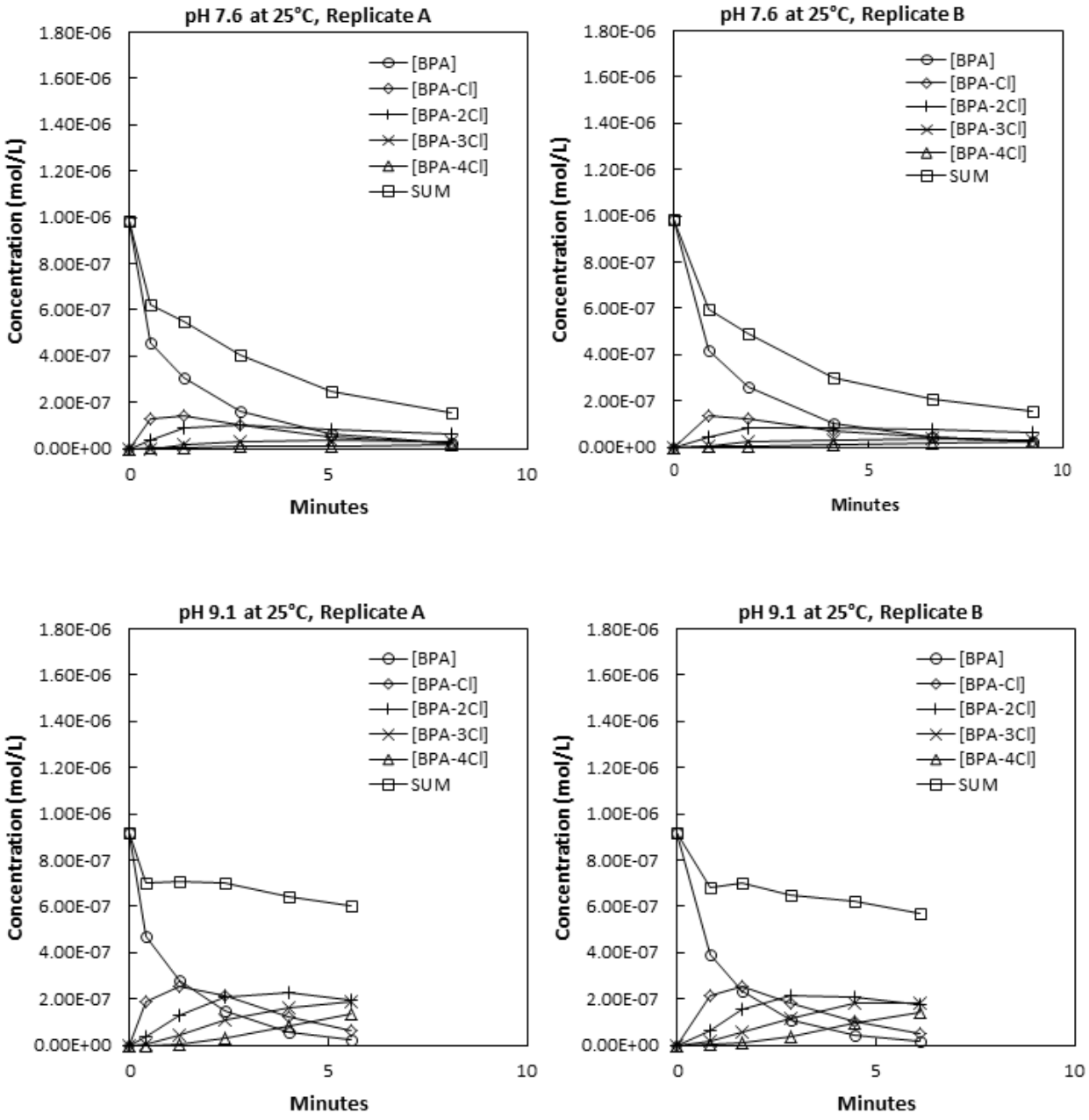


Figure A.4.2.1 BPA decay and the formation of chlorinated by-products during the oxidation of BPA with free chlorine ($HOCl/OCl^-$) at pH 7.6 and 9.1 at 25 °C. Free chlorine concentration averaged 2.1 mg/L (as Cl_2) at pH 7.6 and 2.4 mg/L (as Cl_2) at pH 9.1. Both experiments were run in duplicate and each replicate is shown.

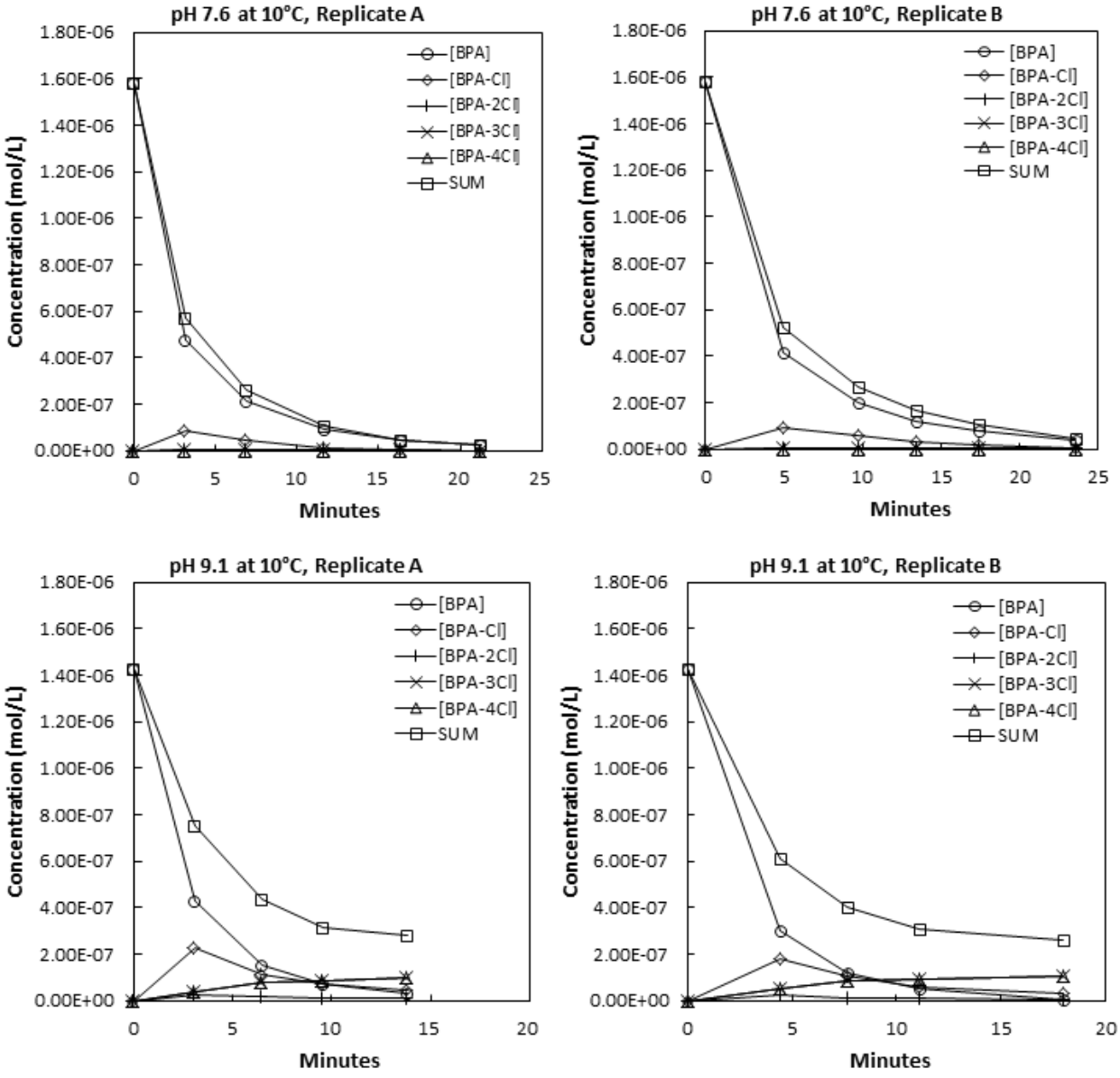


Figure A.4.2.2 BPA decay and the formation of chlorinated by-products during the oxidation of BPA with free chlorine ($HOCl/OCl^-$) at pH 7.6 and 9.1 at 10 °C. Free chlorine concentration averaged 2.1 mg/L (as Cl_2) at pH 7.6 and 2.4 mg/L (as Cl_2) at pH 9.1. Both experiments were run in duplicate and each replicate is shown.

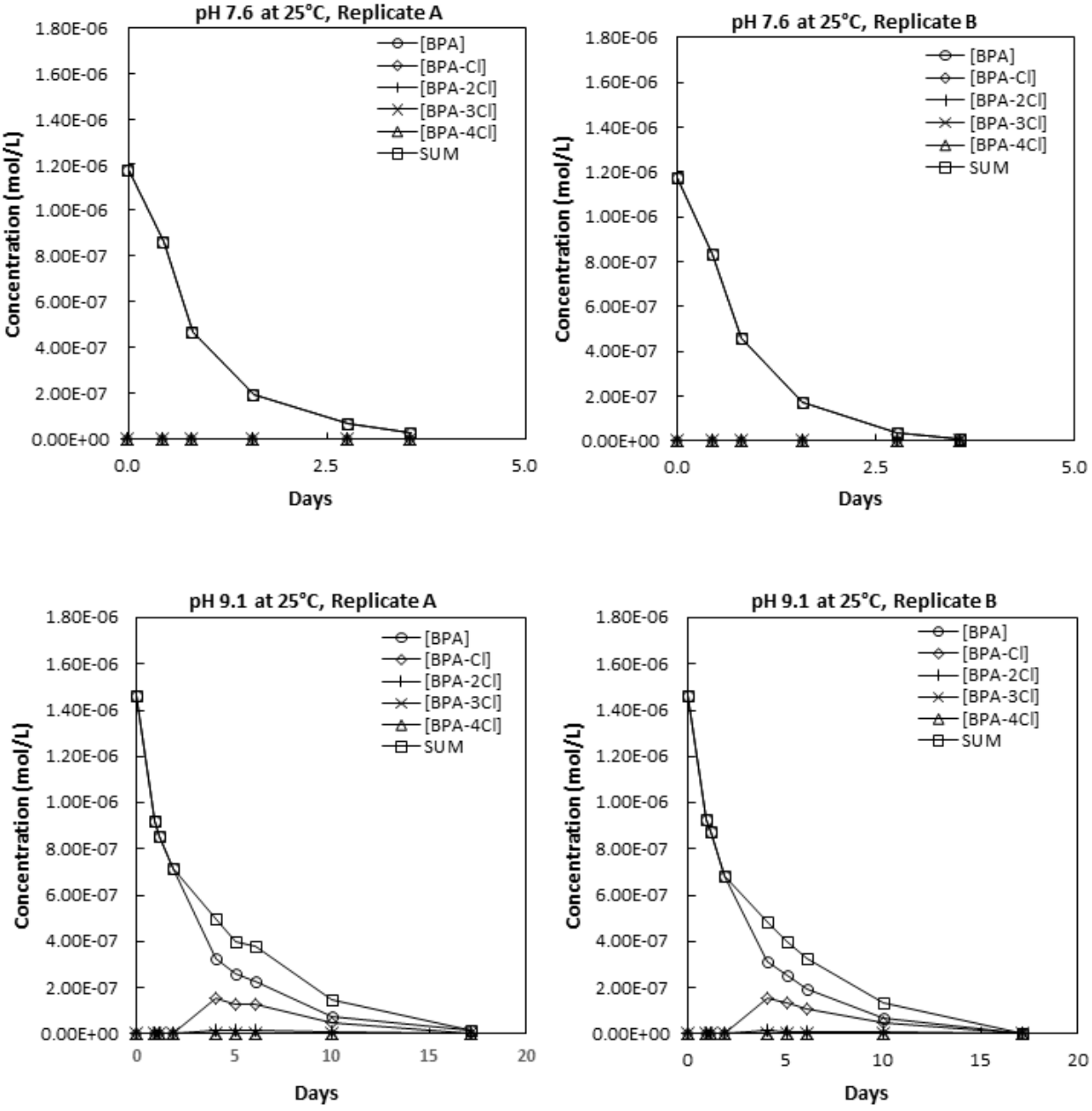


Figure A.4.2.3 BPA decay and the formation of chlorinated by-products during the oxidation of BPA with monochloramine (NH_2Cl) at pH 7.6 and 9.1 at 25 °C. Monochloramine starting concentration averaged 3.7 mg/L (as Cl_2) at pH 7.6 and 3.7 mg/L (as Cl_2) at pH 9.1. Both experiments were run in duplicate and each replicate is shown.

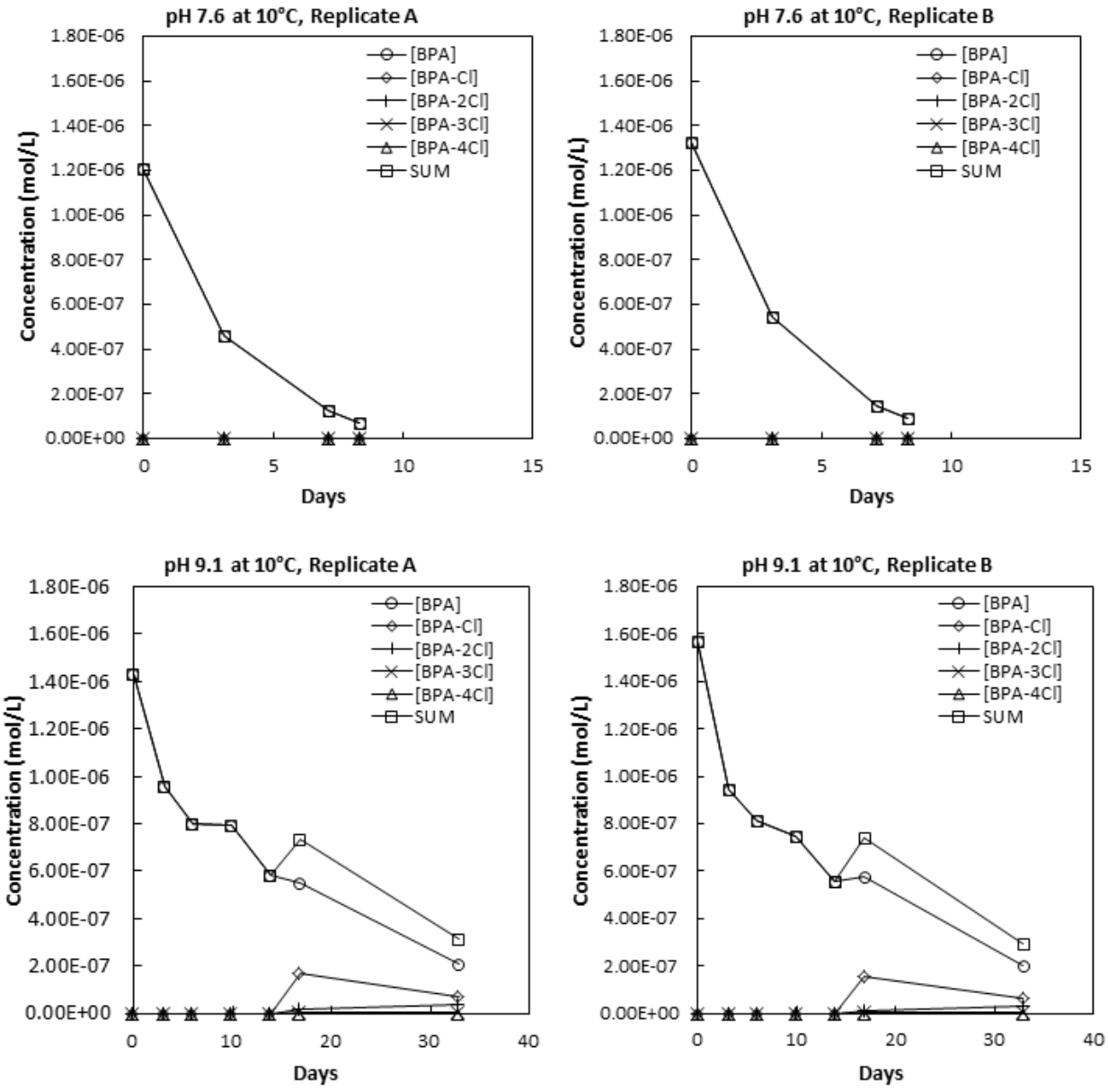


Figure A.4.2.4 BPA decay and the formation of chlorinated by-products during the oxidation of BPA with monochloramine (NH_2Cl) at pH 7.6 and 9.1 at 10 °C. Monochloramine starting concentration averaged 3.7 mg/L (as Cl_2) at pH 7.6 and 3.7 mg/L (as Cl_2) at pH 9.1. Both experiments were run in duplicate and each replicate is shown.